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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C07F 7/08, C07C 63/72, 47/55 C07C 21/24, C07D 303/08 C07C 25/18, C08G 59/38 C08K 5/00	A1	**(11) International Publication Number:** WO 86/ 01511 **(43) International Publication Date:** 13 March 1986 (13.03.86)

(21) International Application Number: PCT/US85/01312

(22) International Filing Date: 11 July 1985 (11.07.85)

(31) Priority Application Number: 646,999

(32) Priority Date: 4 September 1984 (04.09.84)

(33) Priority Country: US

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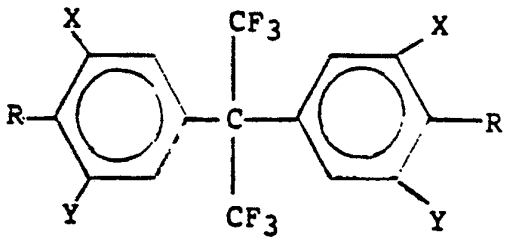
(81) Designated States: CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DERIVATIVES OF DIPHENYLHEXAFLUOROPROPANE



(I)

(57) Abstract

Derivatives of diphenylhexafluoropropane having formula (I) where R is an alkyl, alkylene, carbonyl, carboxy, acyl, aryl, epoxy, silyl or siloxy group; and where X and Y are hydrogen or halogen. The derivatives are useful in formulating polymer structures.

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DERIVATIVES OF DIPHENYLHEXAFLUOROPROPANE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to diphenylhexafluoropropane derivatives and, more particularly, to derivatives wherein various groups are attached to the para-position on the phenyl rings of the diphenylhexafluoropropane by way of a carbon or silicon attachment.

2. Description of the Background Art

Diphenylhexafluoropropane is a very versatile compound which basically consists of two phenyl rings which are attached on opposite sides of the number two carbon of hexafluoropropane. In the past, a number of different derivatives of diphenylhexafluoropropane have been produced by attaching various different functional groups at either the para- or the meta- positions on the phenyl rings. These derivatives have proven to be useful intermediates in the synthesis of thermally stable resins for use in high temperature structural composites.

Diphenylhexafluoropropane compounds have been produced where various different functional groups, such as ethynyl groups, amino groups, or halogens, are attached to the phenyl rings at the meta- position by way of carbon or nitrogen linkages. As is well known, the

specific isomeric form of chemical precursors and intermediates is an important factor in determining the final characteristics and performance of the desired chemical product. Accordingly, it has been desirable to also prepare diphenylhexafluoropropane derivatives in which the functional groups are attached to the phenyl rings at the para- position instead of the meta- position.

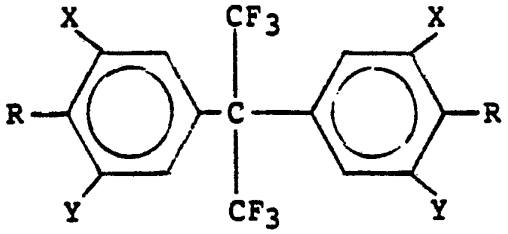
Diphenylhexafluoropropane compounds having an ethynyl group attached at the para- or meta- position have been developed and are disclosed in U.S. Patent No. 4,374,291, which is assigned to the present assignee. However, other para-substituted diphenylhexafluoropropane derivatives which have been developed in the past and which are presently available all include an oxygen or sulfur linkage between the functional group and the phenyl ring. The attachment of the functional groups to the para-position on the phenyl rings via sulfur or oxygen results in a relatively flexible linkage which, in turn, tends to produce relatively flexible polymer products. Although flexible high temperature polymers are well suited for a variety of applications, it is many times desirable to provide thermally stable resins which have increased rigidity. Further, sulfur and oxygen linkages in polymer resins are more susceptible to oxidative degradation or breakdown resulting in premature deterioration of the polymer in which the sulfur or oxygen linked diphenylhexafluoropropane derivative is incorporated.

Therefore, there is a present need to provide para-substituted diphenylhexafluoropropane derivatives which can be used as alternate polymer precursors to meta-substituted derivatives and which do not include a sulfur or oxygen linkage between the para-substituted group and the phenyl rings.

SUMMARY OF THE INVENTION

In accordance with the present invention, a new group of para-substituted diphenylhexafluoropropane compounds are disclosed which provide an alternative polymer precursor to the meta-substituted diphenylhexafluoropropane derivatives while not requiring an oxygen or sulfur linkage.

The new diphenylhexafluoropropane derivatives have the following formula:



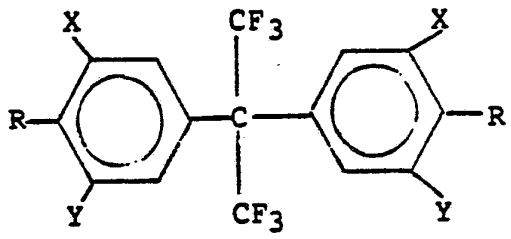
where R is an alkyl, alkylene, carbonyl, carboxy, acyl, aryl, epoxy, silyl or siloxy group; and where X and Y are hydrogen or halogen.

The diphenylhexafluoropropane derivatives in accordance with the present invention have a direct carbon or silicon linkage between the functional groups R and the phenyl rings of the diphenylhexafluoropropane. Carbon or silicon linkages are more rigid than sulfur or oxygen. As a result, more rigid polymers can now be produced from para-substituted diphenylhexafluoropropane than was previously possible with prior sulfur and oxygen linked derivatives. The new diphenylhexafluoropropane derivatives are not only useful in preparing rigid polymers, but the resulting polymers are also thermally stable and resistant to oxidative attack due to the absence of sulfur or oxygen linkages.

The above-discussed and many other features and attendant advantages of the present invention will become better understood by reference to the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The compounds in accordance with the present invention have the following general formula



where R is an alkyl, alkylene, carbonyl, carboxy, acyl, aryl, epoxy, silyl or siloxy group; and where X and Y are hydrogen or halogen.

Preferred alkyl groups are those having from 1 to 4 carbon atoms with methyl being particularly preferred. Preferred alkylene groups also include from 1 to 4 carbon atoms. Vinyl and vinyl derivative groups are particularly preferred. These groups include vinyl, vinyl chloride, propylene, vinyl acetate, styrene, isobutylene, vinylidene chloride or methylmethacrylate and modified acrylics.

Preferred carbonyl groups include aldehydes and ketones having from 1 to 4 carbon atoms with formyl being particularly preferred. Preferred carboxy and acyl groups will have from 1 to 4 carbon atoms with 1 to 2 carbon atoms being particularly preferred. Aryl groups having 1 or 2 phenyl rings are preferred. Silyl and siloxy group having from 1 to 4 carbon atoms are preferred with trimethylsilyl being particularly preferred. In addition, any of the above-mentioned alkyl, alkylene, carbonyl, carboxyl, silyl, siloxy or acyl groups may include one or two phenyl rings.

In addition to the R groups attached at the para-position, the new compounds may include a halogen substituted at the meta-position. Any of the halogens may be used with iodine and bromine being preferred.

Both X and Y may be a halogen if desired; however, it is preferred that when X is a halogen, Y is hydrogen. Also preferred are compounds where both X and Y are hydrogen.

The preparation of compounds in accordance with the present invention preferably begins with 2,2-bis(4-bromophenyl)hexafluoropropane (BPHP). BPHP is a reactive monomer which is the subject of U.S. Patent No. 4,503,254, which has been assigned to the same assignee of the present invention. Although the preferred starting material is bromine substituted, other para-halogenated substituted compounds, such as 2,2-bis(4-iodophenyl)hexafluoropropane and 2,2-bis(4-chlorophenyl)hexafluoropropane, may be used.

The 2,2-bis(4-bromophenyl)hexafluoropropane which is the starting compound in most of the following examples is prepared by reacting triphenylphosphine dibromide with Bisphenol AF [2,2-bis(4-hydroxyphenyl)-hexafluoropropane] at temperatures above 280°C. Bisphenol AF is a common compound which is widely available commercially. An exemplary synthesis is as follows:

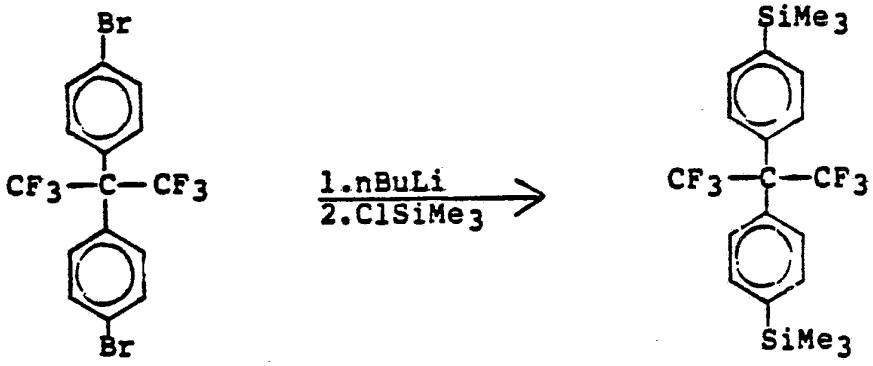
To a slurry of triphenylphosphine dibromide (0.2 mole) in dichloromethane (250 ml) under argon was added 2,2-bis(4-hydroxyphenyl)hexafluoropropane (0.1 mole). The solvent was removed by distillation to leave a solid reaction mixture, and the flask which contained the reaction mixture was placed in a molten metal bath at 350°C for two hours. The reaction mixture was cooled to 100°C and poured into another flask. Further cooling of the reaction mixture resulted in a solid within the flask which was washed three times with 300 ml portions of hexane, and the hexane solution was filtered

to remove unwanted reaction by-products. The resulting hexane solution of the product was washed with 20% sodium hydroxide and deionized water. The solution was then dried over anhydrous magnesium sulfate and passed down a short alumina column. The hexane was removed from the solution and the resulting semi-solid was distilled to produce a 76% yield of the product 2,2-bis(4-bromophenyl)hexafluoropropane, which is a high yield for reactions of this nature.

Examples of preparation of preferred diphenylhexafluoropropane derivatives are as follows:

Example 1:
2,2-bis(4-trimethylsilylphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



To a solution of 4.62g (0.1 mole) 2,2-bis(4-bromophenyl)hexafluoropropane in 75 ml of anhydrous tetrahydrofuran was added dropwise 28 ml (0.4 moles) of a 1.4 molar solution of n-butyllithium in hexane while the reaction mixture was cooled in a dry ice-acetone slush. The reaction mixture was stirred for one half hour at -78°C. A dropwise addition of chlorotrimethylsilane (5 ml, 0.04 moles) was then made to the reaction mixture at -78°C. The stirring slurry was allowed to come to ambient temperature over 16 hours. To the reaction mixture was added 100 ml hexane. The organic layer was

washed with 2 x 150 ml saturated sodium chloride solution and 2 x 150 ml water. The organic layer was dried, filtered, and concentrated to yield the white crystalline product 2,2-bis(4-trimethylsilylphenyl)hexafluoropropane.

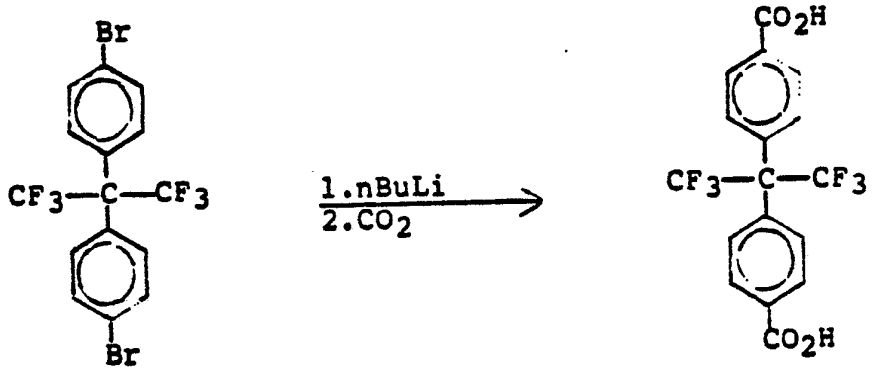
The following physical data were recorded:

NMR ($CDCl_3$): δ 7.4 (m, 4H, aromatic) and 0.5 ppm (s, 9H, silylmethyl).

IR (film): 2970, 1325, 1255, 1210, 1180, 970, 840, 815 cm^{-1}

Example 2: 2,2-bis(4-carboxyphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



To a solution of 23.1 g (0.05 mole) 2,2-bis(4-bromophenyl)hexafluoropropane in anhydrous tetrahydrofuran chilled to -78°C was added dropwise 0.11 moles (78 ml of a 1.4 molar hexane solution) n-butyllithium under an inert gas blanket. The reaction mixture was stirred for 30 minutes at -78°C after the n-butyllithium addition was complete. An excess of carbon dioxide was bubbled through the reaction mixture as the mixture was warmed to 25°C over 16 hours. The thick white slurry was suspended in hexane, filtered, and dried to give 16.53g (0.42 moles, 84% yield). An analytical sample was prepared by recrystallizing 5g of the product from 50 ml glacial acetic acid to give 3.4g of purified 2,2-bis(4-carboxyphenyl)hexafluoropropane. M. P. 268-271°C.

The following data were recorded:

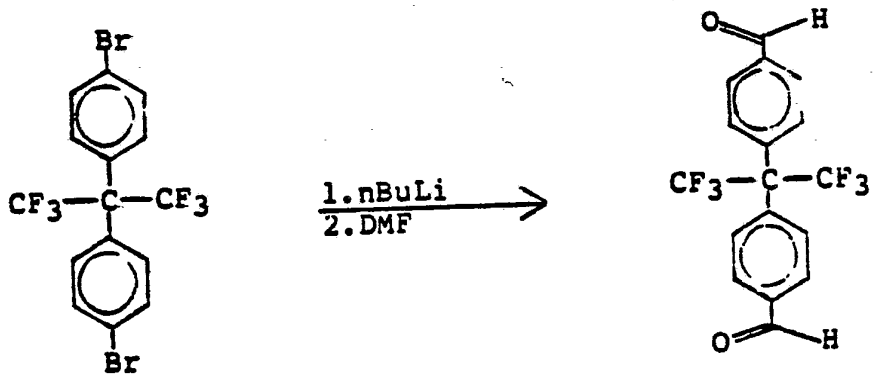
IR (KBr): 2900-3300 (broad), 1705, 1260, 1218, 1180 cm^{-1}

NMR ($CDCl_3$): δ 8.8 (bs, 1H, acid proton) 8.2, 8.1, 7.65, 7.5 ppm (distorted AA' BB' quartet, 4H, aromatic).

Elemental Analysis:		C	H	F
$C_{17}H_{10}F_6O_4$ (392.251)	Calc.	52.06	2.57	29.06
	Found	51.85	2.64	29.37

Example 3: 2,2-bis(4-formylphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



To a solution of 17.58g (0.38 moles) of 2,2-bis(4-bromophenyl)hexafluoropropane in 100 ml anhydrous tetrahydrofuran (THF) at -70°C was added dropwise 83 ml of a 1.1 molar solution in hexane of n-butyllithium. The addition took thirty minutes. After 15 minutes at -60 to -65°C, a dropwise addition of 10.0g (0.137 mole) of dimethylformamide in 50 ml anhydrous tetrahydrofuran was made to the reaction mixture. The reaction mixture was warmed to 25°C over one hour and maintained at 25°C for eighteen hours. At the end of this period, the reaction mixture was poured into 1 liter of stirred water. The product was extracted with ethyl ether, washed with 2 x 200 ml water and the ethereal layer

dried. Concentration of the ethereal fraction afforded 8.46g (23.5 moles, 61.8% yield) of the white solid product 2,2-bis(4-formylphenyl)hexafluoropropane. M. P. 130-132°C.

The following physical data were recorded:

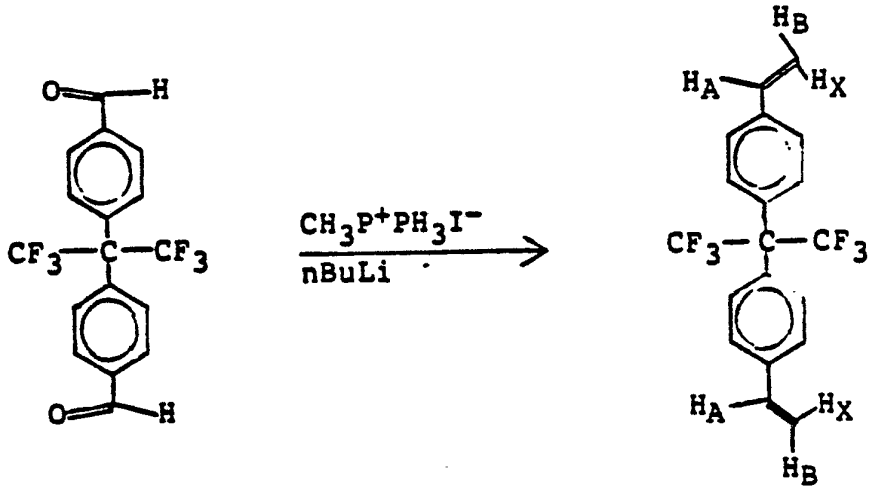
NMR ($CDCl_3$): δ 10.1 (s, 1H, aldehydic proton), and 7.7 ppm (m, 4H, aromatic).

IR (KBr): 1700, 1385, 1315, 1280, 1250, 1230, 1210, 1190, 1170, 1115, 810 cm^{-1}

Elemental Analysis:		C	H	F	Br
$C_{17}H_{10}F_6O_2$ (360.253)	Calc.	56.68	2.80	31.64	0.0
	Found	56.82	2.90	31.47	0.23

Example 4: 2,2-bis(4-vinylphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



Methyl triphenylphosphonium iodide (8.08g) was suspended in 50 ml anhydrous tetrahydrofuran under argon. After cooling to -78°C the slurry was treated with 20 ml (24 mMoles) of 1.2M n-butyllithium. After stirring for 15 minutes, a solution of the dialdehyde product from Example 3 in 40 ml tetrahydrofuran was

added to the slurry still at -78°C. After completion of the addition, the reaction mixture was warmed to 25°C over two hours and maintained at this temperature for 20 hours. The reaction mixture was poured into 500 ml of 10% hydrochloric acid. The product was extracted by four 100 ml ether washes. The combined ethereal extracts were washed with 200 ml of saturated sodium chloride solution and dried over magnesium sulfate. Concentration of the dried ether solution yielded a yellow oil. Column chromatography of this oil using silica gel and 10% methylene chloride in hexane yielded 1.370g (38.5% yield) of a clear yellow viscous oil which was determined to be 2,2-bis(4-vinylphenyl)-hexafluoropropane.

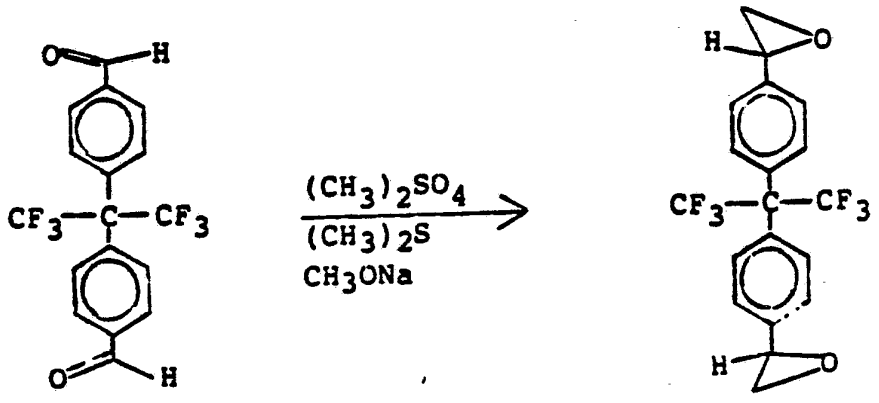
The following physical data were recorded:

GC-MS: one peak, m/e 356

NMR ($CDCl_3$): δ 7.3 (bs, 4H, aromatic H's), 6.9, 6.7, 6.6, 6.5 (d x d, 1H, J_{AB} = 17.5Hz, J_{AC} = 11 Hz, vinyl H_A), 5.8, 5.6, (d x d, 1H, J_{AB} = 17.5Hz, J_{BC} = 1.5 Hz, vinyl H_B), and 5.3, 5.1 ppm (d x d, 1H, J_{AC} = 11 Hz, J_{BC} = 1.5Hz, vinyl H_C). The three vinyl protons give a classical ABX three-nuclei splitting pattern.

Example 5: 2,2-bis(4-epoxyphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



In a flask with an argon atmosphere was placed 3.78g (0.03 mole) dimethyl sulfate, 1.05g (0.033 mole) dimethyl sulfide, and 20 ml acetonitrile. The mixture was stirred 24 hours at 25°C. Sodium methoxide (1.87g, 0.033 mole) was added in one portion and the reaction mixture stirred another hour at 25°C. To the reaction mixture was then added 3.60g (0.01 mole) 2,2-bis(4-formylphenyl)hexafluoropropane, formed as in Example 3, over 15 minutes. After the addition was complete, the stirring was maintained for 18 hours. The reaction flask was then equipped for distillation and the majority of the dimethyl sulfide and dimethyl sulfate removed. To the cooled reaction product was added 20 ml acetonitrile. The organic layer was washed with 4 x 100 ml deionized water, dried over magnesium sulfate, concentrated, and purified using a Kugelrohr apparatus to obtain 2.21g, 0.0057 moles, 57% yield of the product 2,2-bis(4-epoxyphenyl)hexafluoropropane.

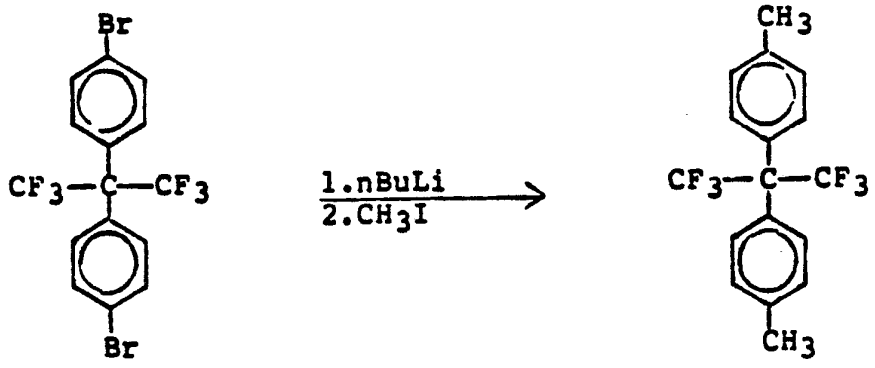
The following physical data were recorded:

IR (film): 1270, 1250, 1215, 1185, 975, 885, 835 cm^{-1}

NMR ($CDCl_3$): δ 7.3 (s), 5.6 (s), 3.8 (m), 3.1 (m), 2.7 (m) ppm

Example 6: 2,2-bis(4-methylphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



A solution was prepared containing 58.78g (0.127 mole) 2,2-bis(4-bromophenyl)hexafluoropropane in 250 ml anhydrous tetrahydrofuran under an argon atmosphere. The solution was cooled to -78°C in a dry ice-acetone slush bath. To the cooled solution was added dropwise 0.28 mole n-butyllithium (112 ml of a 2.5 molar solution in hexane) over a 15 minute period. The solution was stirred for 30 minutes at approximately -78°C after the addition was complete. Cooling of the reaction mixture was continued while adding dropwise 39.7g (0.28 moles) methyl iodide over a 30 minute period. Stirring and cooling was maintained for one hour after the completion of the addition. Then the slush bath was removed and the reaction mixture gradually warmed to ambient temperature. The reaction mixture was washed with 2 x 250 ml of each of the following: saturated sodium chloride solution, dilute sodium bisulfite solution, and deionized water. The organic layer was concentrated to an oil. Recrystallizing the oil from hexane cooled to -78°C yielded 28.25g (0.085 moles, 67% of theory) of the product 2,2-bis(4-methylphenyl)hexafluoropropane. M. P. 76-77°C.

The following physical data were recorded:

IR (KBr): 2990, 2970, 1525, 1265, 1215, 1180 cm^{-1}

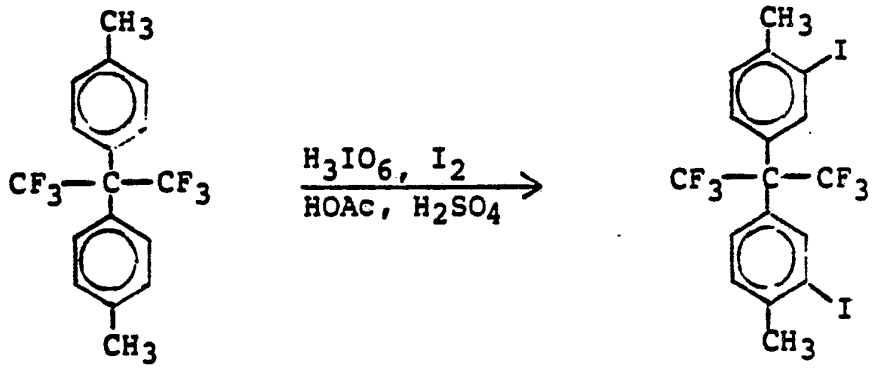
NMR ($CDCl_3$): δ 7.2 (s), 2.3. (s) ppm

Elemental Analysis:	C	H	F
$C_{17}H_{14}F_6$ (332.287)	61.45	4.25	34.30
	6.64	4.40	34.51

Example 7:

2,2-bis(3-iodo-4-methylphenyl)hexafluoropropane

The synthesis is shown schematically as follows:



In a reaction flask equipped with a condenser, 2,2-bis(4-methylphenyl)hexafluoropropane (9.960g), prepared as in Example 6, iodine (12.304g), periodic acid (5.785g), 150 ml glacial acetic acid, 10 ml water, and 3 ml of sulfuric acid were stirred vigorously and heated at 85-90°C for 72 hours. The reaction mixture was cooled and poured into 500 ml of water. The aqueous reaction mixture was extracted with 300 ml of ether. The ethereal phase was washed with sodium bisulfite solution to remove iodine, then 200 ml of water, 200 ml saturated sodium bicarbonate solution, 200 ml of water, and finally dried over anhydrous magnesium sulfate. Concentration of the ethereal phases and recrystallization from pentane yielded the product 2,2-bis(3-iodo-4-methylphenyl)-hexafluoropropane, a white powdery solid. M. P. 101-102°C. in 45% yield.

The following physical data were recorded:

NMR ($CDCl_3$): δ, 7.8 (s), 7.2 (s), 2.4. (s) ppm

MS: (70eV) m/e 584

Elemental Analysis:		C	H	F
$C_{17}H_{12}F_6I_2$ (584)	Calc.	34.96	2.07	43.45
	Found	35.27	2.08	43.23

The diphenylhexafluoropropane derivatives of this invention are useful in a large number of applications. The vinyl and epoxy derivatives may be used alone to produce resin systems or they may be blended with known commercial resins such as any of the vinyl, styrene, butadiene or similar common resins. The ease of vinyl and epoxy polymerization and the special structural characteristics of the vinyl (Example 4) and epoxide (Example 5) derivatives of the present invention jointly provide a facile entry to vinyl and epoxy resins which have the desirable low dielectric constant and low dissipation loss properties for electronic applications. The aldehyde and acid derivatives may be readily incorporated into acetals, polyesters, polyimides, polyimines, polybenzimidazoles, polybenzisoxazoles, polybenzothiazoles, and other polymer classes. In addition, the derivatives may be useful as reactive intermediates in the production of fluorocarbon based pharmaceuticals as well as other organic products.

Exemplary polymers which can be made utilizing the diphenylhexafluoropropane derivatives and the methods for preparing them are as follows:

Example 8: Preparation of polybenzisoxazole containing the hexafluoropropane group

A low molecular weight polymer was prepared by reacting 2,2-bis(4-formylphenyl)hexafluoropropane (see Example 3) and 2,2-bis-(3-amino-4-hydroxyphenyl)-hexafluoropropane in polyphosphoric acid at 200°C for 4 hours. The latter compound was prepared as described

in the publication by K. S. Y. Lau, et al., entitled "Synthesis of Polymer Intermediates Containing the Hexafluoroisopropylidene Group via Functionalization of 2,2-Diphenylhexafluoropropane," in the Journal of Polymer Science: Polymer Chemistry Edition, Vol. 20, 1982, pages 2381-2393.

The mixture was poured into 1 liter of water to precipitate the polymer. After drying at 100°C for 24 hours, the polymer could be purified further by dissolving in N-isopropylpyrrolidinone (NIP) (available from GAF Corporation) and reprecipitating from a hexane-dichloromethane mixture. Inherent viscosity (measured in NIP) was 0.17.

Example 9: Copolymer of Epoxidized Polybutadiene and 2,2-bis(4-epoxyphenyl)hexafluoropropane

Commercially available epoxidized polybutadiene (from Nisso Company, 8% epoxidation of the 90% vinyl pendent groups) was blended with 20% of 2,2-bis(4-epoxyphenyl)hexafluoropropane prepared as in Example 5 and then cured inside a mold with 4% 1,2,3,6-tetrahydrophthalic anhydride and 1% dicumyl peroxide according to a standard multi-stage curing process to form a cured disc copolymer material.

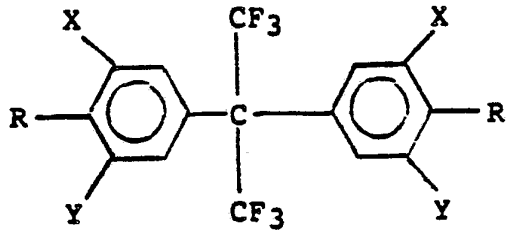
Having thus described exemplary embodiments of the present invention, it should be noted by those skilled in the art that the within disclosures are exemplary only and that various other alternatives, adaptations and modifications may be made within the scope of the present invention. Accordingly, the present invention is not limited to the specific embodiments as illustrated herein and is only limited by the following claims.

MEL:tp
[207-5]

CLAIMS

What is Claimed is:

1. A diphenylhexafluoropropane compound having the formula:



where R is an alkyl, alkylene, carbonyl, carboxy, acyl, aryl, epoxy, silyl or siloxy group; and where X and Y are hydrogen or a halogen.

2. A diphenylhexafluoropropane compound according to Claim 1 where R is a methyl group.

3. A diphenylhexafluoropropane compound according to Claim 1 where X is a halogen and Y is hydrogen.

4. A diphenylhexafluoropropane compound according to Claim 2 where X is a halogen and Y is hydrogen.

5. A diphenylhexafluoropropane compound according to Claim 4 where X is iodine.

6. A diphenylhexafluoropropane compound according to Claim 1 where R is ethylene, vinyl chloride, propylene, vinyl acetate, styrene, isobutylene, vinylidene chloride, or methylmethacrylate.

7. A diphenylhexafluoropropane compound according to Claim 1 where R is an alkyl, alkylene, or alkylene group having from 1 to 4 carbon atoms.

1 8. A diphenylhexafluoropropane compound according to Claim 1 where R is trimethylsilyl.

1 9. A diphenylhexafluoropropane compound according to Claim 1 where R is a carboxyl group having from 1 to 4 carbon atoms.

1 10. A diphenylhexafluoropropane compound according to Claim 1 where R is an aldehyde.

1 11. A diphenylhexafluoropropane compound according to Claim 1 where R is a ketone having from 1 to 4 carbon atoms.

1 12. A diphenylhexafluoropropane compound according to Claim 1 where R is an epoxy group having from 1 to 4 carbon atoms.

1 13. A resin material consisting essentially of a polymer selected from the group consisting of vinyl, styrene and butadiene having incorporated therein a compound according to Claim 6.

1 14. A resin material consisting essentially of a polymer selected from the group consisting of vinyl, styrene and butadiene having incorporated therein a compound according to Claim 12.

1 15. A resin material according to Claim 14 wherein said polymer is epoxidized polybutadiene and said compound is 2,2-bis(4-epoxyphenyl)hexafluoropropane.

1 16. A polymer having incorporated therein a compound acording to Claim 1.

17. A polymer selected from the group consisting of acetal, polyester, polyimide, polyimine, polybenzimidazole, polybenzisoxazole and polybenzothiazole having incorporated therein a compound according to Claim 10.

18. A polymer selected from the group consisting of acetal, polyester, polyimide, polyimine, polybenzimidazole, polybenzisoxazole and polybenzothiazole having incorporated therein a compound according to Claim 9.

19. A polymer consisting essentially of a polybenzisoxazole having incorporated therein a compound according to Claim 10.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/01312

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 07 F 7/08; C 07 C 63/72; C 07 C 47/55; C 07 C 21/24; C 07 D 303/08; C 07 C 25/18; C 08 G 59/38; C 08 K 5/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]			
Classification System	Classification Symbols		
IPC[4]	C 07 F 7/00	C 07 C 21/00	
	C 07 C 63/00	C 07 D 303/00	C 08 G 59/00
	C 07 C 47/00	C 07 C 25/00	C 08 K 5/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3310573 (D.G. COE) 21 March 1967, see examples 1-2; column 1, paragraph 1 --	1-2,7,9,13-19
X	GB, A, 1228007 (E.I. DU PONT DE NEMOURS) 15 April 1971, see examples F,G; claims --	1-2,7,9,13-19
X	Chemical Abstracts, volume 75, no. 3, 19 July 1971, Columbus, Ohio, (US), see page 419, abstract no. 19893p & SU 292948, 15 January 1971 --	1,10
X	EP, A, 0092310 (HUGHES AIRCRAFT COMPANY) 26 October 1983, see claims --	13-19
X	EP, A, 0030432 (DAIKIN KOGYO CO. LTD.) 17 June 1981, see pages 1-4 --	13-19
X	Journal of Polymer Science - Polymer Chemistry Edition, volume 20, 1982, New York, (US) K.S.Y. Lau et al.:"Synthesis of polymer-	

* Special categories of cited documents: [16]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11th December 1985	03 FEV. 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	G.L.M. Kruydenberg

Form PCT/ISA/210 (second sheet) (January 1985)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. [X] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE / partly searchable

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. [ ] Claim numbers....., because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims searched completely : 2,4,5,8,11

Claims searched incompletely : 1,3,7,9,10,12,13-19 } See Annex

Claim not searched : 6

3. [ ] Claim numbers....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. [ ] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. [ ] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

[ ] The additional search fees were accompanied by applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	intermediates containing the hexafluoro isopropylidene group via the functionalization of 2,2- diphenylhexafluoropropane", pages 2381-2393, see page 2381 (cited in the application)	13-19

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 85/01312 (SA 10910)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/01/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3310573		NL-A-	6406896	18/12/64
GB-A- 1228007	15/04/71	None		
EP-A- 0092310	26/10/83	JP-A-	58172330	11/10/83
		US-A-	4503254	05/03/85
EP-A- 0030432	17/06/81	JP-A-	56079150	29/06/81
		US-A-	4339565	13/07/82