SYNTHETIC PROCEDURES TO TETRAALKYS, TETRAACIDS AND DIANHYDRIDES SUBSTITUTED 1,1,1-TRIARYL-2,2,2-TRIFLUOROEthenes Which Comprise:

1. 1,1-bis(dialkylaryl)-1-aryl-2,2,2-trifluoroethane,
2. 1,1-bis(dicarboxyaryl)-1-aryl-2,2,2-trifluoroethane or
3. Cyclic dihydropyridine or dimer of 1,1-bis(dialkylaryl)-1-aryl-2,2,2-trifluoroethanes.

The synthesis of (1) is accomplished by the condensation reaction of an aryltrifluoromethyl ketone with a dialkylaryl compound. The synthesis of (2) is accomplished by oxidation of (1). The synthesis of dihydropyridine (3) is accomplished by the conversion of (2) to its corresponding cyclic dihydropyridine. The synthesis of the diamine is accomplished by the similar reaction of an aryltrifluoromethyl ketone with aniline or alkyl substituted or disubstituted anilines. Also, other derivatives of the above are formed by nucleophilic displacement reactions.

2 Claims, 1 Drawing Sheet
SUBSTITUTED 1,1,1-TRIARYL-2,2,2-TRIFLUOROETHANES AND PROCESSES FOR THEIR SYNTHESIS

ORIGIN OF THE INVENTION

The invention was made by Government employees and may be manufactured or used by or for the Government without the payment of any royalties thereon or therefor.

REFERENCE TO RELATED APPLICATIONS

This application is a division of patent application Ser. No. 924,474 filed Oct. 29, 1986, for "Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes and Processes and Their Synthesis", now U.S. Pat. No. 4,758,380 and is copending with patent application Ser. No. 292,049 entitled "Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes and Processes and Their Synthesis".

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods for the synthesis of substituted 1,1,1-triaryl-2,2,2-trifluoroethanes and to products resulting therefrom, as well as to derivatives derived from said products. The polymeric derivatives of said products meet or exceed the performance characteristics required for high temperature resins and composites in present or future aeronautic requirements.

The utility of polyimides as a class of polymers is well-known. Polyimides, because of their low cost, excellent thermo-oxidative stability, chemical stability, and commercial availability, are in a class by themselves. They exhibit widespread applications, such as for films, coatings, moldings, adhesives, binder solutions and matrix resins. Extensive review articles and books, such as in Heat-Resistant Polymers, J. P. Critchley, et al, chapter 5, on Polyimides, (Plenum Press, 1983) describe the many polyimides that have been prepared and indicate which compositions are successful commercial variants. In a class by themselves are the fluorinated containing 1,1,1,3,3,3-hexafluoroisopropylidene (6F) polyimides because of their superior thermal stability compared to non-fluorinated polyimides. The 6F containing polyimides have become the state-of-the-art in melt processable polyimides for moldings and matrix resin applications. This patent application is designed to show new synthetic routes for the new 1,1,1-triaryl-2,2,2-trifluoroethane (3F) containing monomers which will exhibit all the desirable melt fusible-melt processable characteristics of 6F containing monomers but in addition are more versatile than 6F containing monomers because of the potentials described to introduce a variety of functional groups for the modification of polymer properties. In addition, this disclosure claims a variety of methods to effect the functional group introduction, such as from during the initial monomer synthesis, to during a later step in the monomer synthesis, to performing functional group changes on the final polymer structure. The copending Lew 14,346-1 disclosure generally claims the polymerization to new 3F polyimides after the functional groups for modifying polymer properties are already within the monomer structure but is not limited to introduction of functional groups prior to polymerization. Changes in functional groups may be effected once a functional group already exists without a 3F containing polymer.

2. Description of the Prior Art

Presently, one method of meeting high temperature performance requirements has been through the use of commercially available thermo-oxidatively stable monomers/polymers based on a 2,2-diaryl-1,1,3,3,3-hexafluoroisopropylidene structure (6F). A 1,1,1-triaryl-2,2,2-trifluoroethane structure (3F) is also known.

The synthesis of dianhydrides and diamines based on similar 6F structures has been previously reported as follows and is described within examples in U.S. Pat. No. 3,310,573, which issued on Mar. 21, 1967.

CH$_3$ + CF$_3$CCF$_3$ → HF → CF$_3$C(O)CF$_3$ → CF$_3$C(=O)CF$_3$ → CF$_3$C(=O)CF$_3$ (example I)

chromic acid oxidation

CF$_3$C(=O)CF$_3$ → CF$_3$C(=O)CF$_3$ (example II)

hydrazoic acid → CF$_3$C(=O)CF$_3$ (example III)

6F Diamine (example III)
The dianhydride of example IX of U.S. Pat. No. 3,310,573 is presently used in commercially available resin products (called NR 150 resins) available from E. I. duPont. The 6F dianhydride and 6F diamine monomers are also presently available in developmental quantities from American Hoechst. A similar 6F diamine with meta, rather than para, substitution has been recently synthesized, K. S. Y. Lau, et al., J. Polymer Science, 20, 2381-2393 (1982), and is also available from American Hoechst in developmental quantities. The synthesis of this diamine is summarized below.

However, neither of the Kray, et al references describe the synthesis of a tetra substituted 3F structure required to prepare a new 3F dianhydride monomer. Nor do these references describe the requirement to use stoichiometric, rather than catalytic, amounts of CF$_3$SO$_3$H condensing agent based on equimolar or greater amounts of CF$_3$SO$_3$H with the aryl trifluoromethyl ketone.
The utility of the synthesis of 3F monomers over state-of-the-art 6F monomers is because the 3F phenyl ring is useful as a synthetic site. This utility creates 3F synthesis technology as the next generation of more synthetically versatile polymers compared to the state-of-the-art 6F polymers currently claimed for specialized applications such as solar cell coatings (U.S. Pat. No. 4,592,925) or radiation-resistant or radiation sensitive modified 6F monomers (U.S. Pat. No. 4,416,973). A further utility of 3F monomers over non-3F or 6F monomers/polymers is in the synthetic procedure to prepare 2,6-substituted and disubstituted 3F diamines for potential use as photoresists. This advances the technology of non-fluorinated photoresists described in J. Pfeifer and O. Rhode of Ciba-Geigy in “Direct Photomaging of Fully Imidized Solvent Soluble Polyimides” in proceedings of 2nd International Conference on Polyimides, 10/30/85-11/1/85 at Ellenville, N.Y.

SUMMARY OF THE INVENTION

Therefore, it is an object of this invention to provide a process for preparing tetraalkyl-substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which comprises reacting an aryl trifluoromethyl ketone with a dialkylaryl compound.

A further object is to provide methods for preparing tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which comprises oxidation of a 1,1-bis(dialkylaryl)-1-aryl-2,2,2-trifluoroethane compound.

A further object is to provide methods for preparing cyclic dianhydrides of 1,1,1-triaryl-2,2,2-trifluoroethane, which comprises conversion of a 1,1-bis(dicarbonylaryl)-1-aryl-2,2,2-trifluoroethane compound to its corresponding cyclic dianhydride.

A further object is to provide a method for preparing diamines of 1,1,1-triaryl-2,2,2-trifluoroethane.

A further object is to provide a method for preparing tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which additionally contain pendant fragments substituted nucleophilically thereon.

Yet further we have discovered that the products resulting from each of the above methods are new.

Further objects of the invention will be apparent from the detailed description of the invention which follows.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Tetraalkyl-Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes

Applicants have discovered a novel process for reacting an aryl trifluoromethyl ketone with a dialkylaryl compound which will result in the formation of a new tetraalkyl-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound.

Suitable aryl trifluoromethyl ketones include those of the formula

wherein Ar=cyclic and polycyclic aromatic hydrocarbons such as benzene, naphthene, phenanthrene, pyrene, anthracene, etc. and X is O (oxygen), S (sulfur), SO₂ (sulfone), NH (nitrogen-hydrogen), PH (phosphorous-hydrogen), N₄ (nitrogen-phenyl), P₄ (phosphorous-phenyl), C=O (carbonyl), CH₂ (methylene) or CH₃ (carbon-hydrogen-phenyl) and the placement of X may be in either the meta or para positions.

Especially preferred is α,α,α-trifluoroacetophenone,
propyl, propyl, t-butyl, n-butyl, isobutyl, etc. The only limitation being that the R,R containing compound be liquid at the reaction temperature to act as the reaction solvent. A general description of the typical aryltrifluoromethyl ketone condensation process is as follows:

An aryltrifluoromethyl ketone, where aryl is a phenyl, polycyclic aromatic hydrocarbon or phenyl with a pendant non-alkyl group attached, is reacted with an excess an ortho-substituted dialkyl aromatic using an equimolar or greater amount (based on moles of aryltrifluoromethyl ketone) of organic superacids, such as trifluoromethyl-sulfonic acid. The solvent for the reaction is always the ortho-substituted dialkyl aromatic. The condensation reaction may be done between 0° C. and the reflux temperature of solvent for anywhere from 1 hour to 7 days, however the preferred choice is at least 2 days at room temperature (20°-25° C.). The product invariably precipitates from the reaction mixture and is isolated by filtration. A second crop of product is often obtained by evaporation of the reaction filtrate. The yields may be from 0 to 100%, but generally range from 70 to 80% of tetraalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes.

Tetracarboxy-substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes

Applicants have also discovered a novel process which comprises oxidation of a tetraalkyl-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound to produce a new tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound.

Suitable tetraalkyl-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compounds include those of the formula:

A general description of a typical oxidation process is as follows:

A tetraalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethane, where one aryl is a phenyl, polycyclic aromatic hydrocarbon or phenyl with a pendant non-alkyl group attached, is oxidized in a two-step oxidation process such as potassium permanganate in pyridine/water followed by in pyridine/alkali or other oxidation processes such as vapor phase oxidation over active metal catalysts such as vanadium pentoxide, or air/liquid phase cobalt acetate/acetic acid oxidations. The permanganate oxidations are done from 50° to 130° C., but typically at the reflux temperature of pyridine/water (~90° C.) for anywhere from 20 minutes to 24 hours, but typically 3 hours. The tetracarboxy product is isolated by acidification of the reaction filtrate and the yields may range from 0 to 100% depending on the ability of the tetraacid to precipitate, but typically are 40 to 70%.
Cyclic Dianhydrides of 1,1,1-Triaryl-2,2,2-Trifluoroethanes

Applicants have also discovered a novel process which comprises conversion of a tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound to its new corresponding cyclic dianhydride.

Suitable tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compounds are 1,1-bis(dicarboxyaryl)-1-aryl-2,2,2-trifluoroethane compounds. Preferred species include those of the formulae:

\[
\begin{align*}
\text{H}_2\text{C} & - \text{C} - \text{H}_2\text{C} \\
\text{HO}_2\text{C} & - \text{C} - \text{CO}_2\text{H} \\
\text{CO}_2\text{H} & - \text{C} - \text{CO}_2\text{H}
\end{align*}
\]

wherein Ar is cyclic and polycyclic aromatics as defined earlier, \( X \) is \( \text{O} \), \( \text{S} \), \( \text{SO}_2 \), \( \text{NH} \), \( \text{PH} \), \( \text{N}_2 \), \( \text{P}_4 \), \( \text{C} = \text{O} \), \( \text{CH}_2 \) or \( \text{CH}_4 \). Especially preferred is

\[
\begin{align*}
\text{HO}_2\text{C} & - \text{C} - \text{CO}_2\text{H} \\
\text{CO}_2\text{H} & - \text{C} - \text{CO}_2\text{H}
\end{align*}
\]

Conversion of the new 3F tetramethyl compound, to the new 3F tetracarboxy intermediate compound, from which the new 3F dianhydride is to be derived, is by customary oxidation procedures with the exception that nitric acid used for similar 6F dianhydrides, pyromellitic dianhydride and benzophenonetetraacarboxylic dianhydride cannot be used (due to nitration of the unsubstituted phenyl ring of the tetramethyl 3F precursor). Instead, oxidation to the 3F tetraacid is accomplished by use of an oxidation catalyst which does not cause nitration, such as potassium permanganate, followed by ring closure with acetic anhydride to the 3F dianhydride as described in Example III.

A general description of a typical acetic anhydride dehydration process is as follows:

A tetracarboxy ortho substituted 1,1,1-triaryl-2,2,2-trifluoroethane, where one aryl is a phenyl, polycyclic aromatic hydrocarbon or phenyl with a pendant non-alkyl group attached, is dehydrated to the corresponding dianhydride by treatment in acetic anhydride, with or without acetic acid added, at any temperature between 40° to 120° C., but typically at the reflux temperature of the acetic anhydride/acetic acid solvent mixture for anywhere from ten minutes to 24 hours, but typically 1–2 hours. The dianhydride is usually isolated by filtration of the cooled reaction solvent and purified by recrystallization and/or sublimation of the reaction product. Additional isolation techniques for soluble dianhydrides are complete evaporation of acetic anhydride/acetic acid reaction solvent.

This synthetic procedure is analogous to small scale laboratory procedures for other tetramethyl compounds such as tetramethyl compounds with a 6F linkage as disclosed in Example IX of U.S. Pat. No. 3,310,573 or an oxygen connecting linkage as in C. S. Marvel, et al., J. Am. Chem. Soc., 80, 1197 (1958).

Because of the commercial development of 6F dianhydride monomer, improved oxidation processes, rather than permanganate oxidation, have presumably been long since developed by both E. I. DuPont, American Hoechst and others. These procedures are presumably vapor phase oxidation such as is done for preparation of pyromellitic dianhydride, W. Flavell, et al., Chem. Brit. 3, 375 (1967), or air/liquid phase cobalt acetate/acetic acid type oxidation technology for which American Hoechst is one of the pioneers, or nitric acid oxidation such as used for synthesis of benzophenone tetracarboxylic dianhydride, French patent No. 1,346,797 (1963) and 6F dianhydride, British patent No. 1,062,435, Mar. 22, 1967.

In the 3F dianhydride case, only permanganate has been successful as an oxidation reagent. Oxidation with nitric acid also leads to nitration of the unsubstituted phenyl ring of the tetramethyl 3F precursor along with oxidation to the tetraacid. Commercial large scale vapor phase or air/liquid phase oxidations have not been optimized as these entail specialized process development and prior expertise in the technology, although this assumedly would be the most successful as these procedures are used for the preparation of 6F dianhydride from 6F tetramethyl precursor.

FIG. 1 illustrates the process step of 6F dianhydride from 6F tetramethyl precursor.
Diamines of 1,1,1-Triaryl-2,2,2-Trifluoroethane

Applicants have also discovered a novel process which comprises reacting

\[
\text{Ar} - \text{CF} = \text{C} - \text{F}_3 \text{ or } \text{Ar} - \text{CF} = \text{C} - \text{Ar}
\]

wherein \( \text{Ar} \) is a cyclic or polycyclic aromatic as defined earlier, \( X \) is \( O, S, \text{SO}_2, \text{NH}, \text{PH}, \text{N}, \text{P}, \text{C}=\text{O}, \text{CH}_2 \text{ or CH}_2 \text{N} \) with aniline or 2,6-substituted or disubstituted anilines

\[
\text{R- Ar-NH}_2 \ 	ext{ and } \text{R'- Ar-NH}_2
\]

where \( \text{R and R'} \) are the same or different and stand for hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, and greater alkyls, in the presence of anilinium hydrochloride or the corresponding 2,6-substituted or disubstituted anilinium hydrochloride condensation agent, based on moles of aryl trifluoromethyl ketone. The solvent for the reaction is always the aniline or 2-substituted aniline or 2,6-disubstituted aniline. The condensation reaction may be done between 120° to 200° C, but generally at the reflux temperature of the solvent (~160° C.) for anywhere from 1 hour to 7 days but generally 10 to 30 hours. The excess aniline or substituted/disubstituted aniline solvent is removed by steam distillation and the diamine product collected by filtration of the then aqueous reaction. The crude yields may be from 0 to 100%, but generally are quantitative (95-100%). The diamines may be purified by recrystallization from solvents such as ethanol or chloroform, but are not limited to these solvents, with or without charcoal treatment, to provide generally 50 to 85% purified yields of 1,1,1-bis[(4-amino-3,5-dialkyl)phenyl]-1-phenyl-2,2,2-trifluoroethanes.

FIG. 2 illustrates a method for preparing a diamine of 1,1,1-triaryl-2,2,2-trifluoroethane.

Derivatives of Tetracarboxy-Substituted 1,1,1-Triaryl-2,2,2-Trifluoroethanes

The applicants claim a novel method for preparing a new compound of the formulae

\[
\text{HO}_2\text{C} - \text{C}_0\text{2H} - \text{HO}_2\text{C} - \text{C}_0\text{2H}
\]

where \( \text{Ar} \), polycyclic aromatic hydrocarbon as described earlier and \( X \) has the same meaning as above and \( \text{R and R'} \) are the same or different and may stand for \( H \) (hydrogen), methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl and greater alkyls. The only constraints placed on the aniline or 2,6-substituted or disubstituted anilines being the amine must be liquid at the reaction temperature to act as the reaction solvent.

wherein \( \text{Ar} \) is a cyclic or polycyclic aromatic hydrocarbon as described earlier and \( X \) has the same meaning as above and \( \text{R and R'} \) are the same or different and may stand for \( H \) (hydrogen), methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl and greater alkyls. The only constraints placed on the aniline or 2,6-substituted or disubstituted anilines being the amine must be liquid at the reaction temperature to act as the reaction solvent.

A general description of a typical aniline or substituted/disubstituted aniline condensation process is as follows:

An aryl trifluoromethyl ketone, where aryl is phenyl, polycyclic aromatic hydrocarbon or phenyl with a pendant non-alkyl group attached, is reacted with excess aniline or excess 2,6-substituted or disubstituted anilines using a stoichiometric or greater amount of a corresponding anilinium or 2,6-substituted or disubstituted anilinium hydrochloride condensation agent, based on moles of aryl trifluoromethyl ketone. The solvent for the reaction is always the aniline or 2-substituted aniline or 2,6-disubstituted aniline. The condensation reaction may be done between 120° to 200° C, but generally at the reflux temperature of the solvent (~160° C.) for anywhere from 1 hour to 7 days but generally 10 to 30 hours. The excess aniline or substituted/disubstituted aniline solvent is removed by steam distillation and the diamine product collected by filtration of the then aqueous reaction. The crude yields may be from 0 to 100%, but generally are quantitative (95-100%). The diamines may be purified by recrystallization from solvents such as ethanol or chloroform, but are not limited to these solvents, with or without charcoal treatment, to provide generally 50 to 85% purified yields of 1,1,1-bis[(4-amino-3,5-dialkyl)phenyl]-1-phenyl-2,2,2-trifluoroethanes.

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The applicants claim a novel method for preparing a new compound of the formulae

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\text{HO}_2\text{C} - \text{C}_0\text{2H} - \text{HO}_2\text{C} - \text{C}_0\text{2H}
\]

where \( \text{Ar} \), polycyclic aromatic hydrocarbon as described earlier and \( X \) has the same meaning as above and \( \text{R and R'} \) are the same or different and may stand for \( H \) (hydrogen), methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl and greater alkyls. The only constraints placed on the aniline or 2,6-substituted or disubstituted anilines being the amine must be liquid at the reaction temperature to act as the reaction solvent.

wherein \( \text{Y} \) is \( \text{O} \) (phenyl-oxygen), \( \text{S} \) (phenyl-sulfur), \( \text{SO}_2 \) (phenyl-sulfone), \( \text{PH} \) (phenyl phosphorous hydrogen), \( \text{P} \) (diphenyl phosphorous), \( \text{NH} \) (phenyl nitrogen hydrogen), \( \text{N} \) (diphenyl nitrogen) or \( \text{NO}_2 \) (nitro). Although \( \text{X} \) shown earlier and some \( \text{Y} \) may appear equivalent, the distinctions are 1) \( \text{X} \) may be meta or para while \( \text{Y} \) is always meta and 2) \( \text{X} \) is incorporated into the aryl trifluoromethyl ketone before synthesis of the 3\text{F} tetraalkyl or 3\text{F} diamine compounds while \( \text{Y} \) is nuleophilically put on the 3\text{F} tetraacid or dianhydride or 3\text{F} diamine after the synthesis. The preparation method described comprises oxidation of
in the presence of HNO₃. Especially preferred is when the oxidized product is the 3-nitro phenyl product shown below and is described in Example V.

A general description of a typical nitric acid oxidation process is as follows: A tetraalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethane, where one aryl is an unsubstituted phenyl, polycyclic aromatic hydrocarbon of phenyl with a pendant non-alkyl group attached, is oxidized in an autoclave with excess 20 to 60% nitric acid, generally 1 to 3 hours. To the reaction mixture is later added up to 5 to 30% by volume of concentrated sulfuric acid, generally 2 to 4 hours, to complete the mononitration of the unsubstituted 3F aryl rings. The mononitrate tetracarboxy 3F containing products are isolated by filtration of the reaction media and washed with water to provide mononitrated tetracarboxy 3F containing products. The nucleophile substituent onto the previously unsubstituted aryl radical of the tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound is initially placed in an ice bath, then left to reach room temperature, generally around 180°C for 30 minutes to 24 hours, generally 1 to 3 hours. The reaction mixture is later added up to 5 to 30% by volume of concentrated sulfuric acid, generally 2 to 4 hours, to complete the mononitration of the unsubstituted 3F aryl rings. The mononitrate tetracarboxy 3F containing products are isolated by filtration of the reaction media and washed with water to provide 40 to 100% yields of product, generally 90-95% of mono nitro 3F tetracarboxylic acids. The nitro products are subject to a nucleophilic displacement reaction comprising reacting said oxidized product to Y radical containing nucleophilic reagents, wherein Y has the same meaning as defined above. An example is given in Example VI.

A general description of a typical nucleophilic displacement reaction process is as follows: A mononitrated tetraalkyl substituted-1,1,1-triaryl-2,2,2-trifluoroethane, where one aryl is the mononitrated phenyl, a mononitrated polycyclic aromatic hydrocarbon or a monophenyl with a pendant non-alkyl group as a nitrated or un-nitrated aromatic attached, is reacted with typical nucleophilic reagents, described as Y. The reaction solvents include, but are not limited to, N-methyl pyrrolidinone, N-methyl formamide, N,N-dimethyl formamide, N,N-dimethyl acetamide, dimethyl sulfoxide and mixtures thereof. The reaction temperatures may be from room temperature to reflux temperature of the solvent used, but generally reflux temperature. Even higher temperatures may also be attained in an autoclave when nucleophilic substitution has not occurred at reflux temperature. Reaction times and yields vary widely depending on reactivity of the nucleophile and range from 30 minutes to 7 days, but generally 2 to 6 hours to obtain yields ranging from 0 to 100%, but generally 30 to 60%. The nucleophilically substituted products are isolated by methods of filtration of the precipitated product from the reaction media, addition of water to precipitate the product followed by filtration and/or evaporation of the reaction solvents. Purification is by recrystallization from solvents which include, but are not limited to, ethanol or chloroform or by conversion to the corresponding diahydride by acetic anhydride treatment and purification of the diacyldride instead.

FIG. 3 illustrates the method for the attachment of a nucleophile substituent onto the previously unsubstituted aryl radical of the tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethane compound.

The following examples are intended to illustrate the invention and are not to be construed as limiting the process.

**EXAMPLES**

This invention is further illustrated by, but not limited to, the following examples.

**EXAMPLE I**

This Example I discloses a method for the preparation of tetralkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which comprises reacting an aryl trifluoromethyl ketone with dialkylaryl compound.

In a 500 ml. round bottom flask equipped with a magnetic stir bar and a drying tube was mixed 359.0 g. (3.38 mole) of o-xylene, 39.5 g. (0.227 mole) of a,a,a-trifluorocacetophenone and (0.230 mole, slightly more than stoichiometric based on aryl trifluoromethyl ketone moles) of trifluoromethane sulfonic acid. For larger scale reactions, the trifluoromethane sulfonic acid is added dropwise over 1-2 hours and the reaction is initially placed in an ice bath, then left to reach room temperature during the addition. The solution was stirred at room temperature for 48 hours during which the product precipitated. After this time, the product was collected by suction filtration, rinsed with o-xylene, followed by three rinsings with water. The filtrate was extracted in a separatory funnel with successive washings with water, aqueous sodium bicarbonate and water.

The o-xylene solution was dried over magnesium sulfate, filtered, evaporated to about 50 ml. and placed in a refrigerator to obtain additional crystalline product, which was collected by suction filtration. The 1,1-bis-[1,2-dimethyl]phenyl]-1-phenyl-2,2,2-trifluoroethane was recrystallized from a 90/10 by volume mixture of heptane/benzene to yield from initial reaction precipitate, 57.2 g. (68.5% yield) of white solid, m.p. 177-178°C. and 4.8 g (5.7% yield) of white solid, m.p. 171-174°C. from the solution after evaporation of the o-xylene reaction solvent.

**EXAMPLE II**

This Example II discloses a method for the preparation of tetracarboxy-substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which comprises oxidation of tetralkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes.

In a 500 ml. 3-neck round bottom flask equipped with a magnetic stir bar and a reflux condenser was mixed 10.00 g. (27.2 mmol) of 1,1-bis-[4-(1,2-dimethyl)phenyl]-1-phenyl-2,2,2-trifluoroethane and 225 ml. of pyridine. The mixture was brought to reflux temperature and 50 ml of water was added. Then 21.48 g (0.136 moles, 5 fold excess) of solid potassium permanganate was added in small portions over 10 minutes. After 3 hours stirring at reflux temperature, the manganese dioxide formed was collected by filtration through Celite and washed with water/pyridine. The yellow filtrate was evaporated to 50 ml., placed back in the 500 ml. flask with 200 ml. of water and 16 g. (0.4 moles) of
This Example V discloses a method for the preparation of nitroalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes, which comprises nitrating the tetraalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes.

In an autoclave is mixed 10.0 g. (27.2 mmoles) of 1,1-bis-[4-(1,2-dicarboxy)phenyl]-1-phenyl-2,2,2-trifluoroethane and 180 g. of 35% nitric acid. The mixture is heated in the sealed autoclave for 2 hours at 180°C and cooled to room temperature. The tetraacid (with some nitrination on the 3F phenyl ring) is seen as a precipitate in the nitric acid reaction media. To this mixture is added cautiously 30 g. of concentrated sulfuric acid and the mixture is heated to at least 50°C for 2 hours, in order to completely mononitritate the 3F phenyl ring. The reaction is cooled to room temperature and the precipitate is collected by filtration, water washed and air dried to yield greater than 90% yields of 1,1-bis-[4-(1,2-dicarboxy)phenyl]-1-(3-nitrophenyl)-2,2,2-trifluoroethane.

EXAMPLE VI

This Example VI discloses a method for the preparation of tetracarboxy substituted 1,1,1-triaryl-2,2,2-trifluoroethanes with pendant fragments on one phenyl ring, which comprises nucleophilic displacement reactions in the nitric acid oxidation products of tetraalkyl substituted 1,1,1-triaryl-2,2,2-trifluoroethanes.

In a 500 ml. round bottom flask equipped with a magnetic stir bar and a reflux condenser is mixed 10.0 g. (24.2 mmoles) of 1,1-bis-[4-(1,2-dicarboxy)phenyl]-1-(3-nitrophenyl)-2,2,2-trifluoroethane 3.0 g. (25.8 mmoles, 7% excess) of sodium phenoxide and 100 ml. of N,N-dimethylformamide. The stirred mixture is heated to the reflux temperature for 3 hours and cooled to room temperature. To the solution is added 40 ml. of water and the precipitated 1,1-bis-[4-(1,2-dicarboxy)phenyl]-1-(3-phenoxypyphenyl)-2,2,2-trifluoroethane is collected by filtration, washed with water and air dried. What is claimed is:

1. A process for preparing a 1,1-bis(dicarboxyaryl)-1-aryl-2,2,2-trifluoroethane compound which comprises oxidation of a 1,1-bis(dialkylaryl)-1-aryl-2,2,2-trifluoroethane compound wherein the 1,1-bis(dialkylaryl)-1-aryl-2,2,2-trifluoroethane is selected from formulae:
wherein Ar is selected from phenyl, naphthalene, phenanthrene, or pyrene, and X is O, S, SO₂, NH, PH, N⁺, P⁺, 0, CH₂ or CH⁺ and R and R' are the same or different and are individually an alkyl radical, the oxidation being carried out in the presence of vanadium pentoxide wherein the oxidation is conducted in vapor phase oxidations or air/liquid phase cobalt acetate/acetic acid oxidation technology.

2. A process according to claim 9, for preparing a compound of the formula:

wherein R and R' are the same or different and are individually an alkyl radical, in the presence of an oxidation catalyst selected from vanadium pentoxide wherein the oxidation is conducted in vapor phase oxidation or air/liquid phase cobalt acetate/acetic acid oxidation systems. * * * *