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IMPROVED METHOD FOR THE PREPARATION OF IODONIUM SALTS

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(56) Prior Art Documents
US 4826635
US 4554360
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(57)

The diaryliodonium salts prepared by our invention are diaryliodonium salts having the general formula $R^i_aArI^+ArR^{ii}_bX^-$.

Claim

1. A method for the preparation of iodonium salts of the formula $R^i_aArI^+ ArR^{ii}_{bx}{}^-$ where R^i is selected from the group consisting of monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms, halogen atoms, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups and alkoxy substituted groups. R^{ii} is selected from the group consisting of hydrogen, monovalent hydrocarbon radicals free of aliphatic unsaturation and having from 1 to 40 carbon atoms, alkoxy radicals, arylalkoxy radicals, aryloxy radicals and halogen atoms, Ar denotes arene radicals having from 6 to 40 carbon atoms, a has a value of from 0 to 10, b has value of from 0 to 10 and X^- is an anion selected from the group consisting of perfluoroalkylsulfonic acid anions, hexahalometallic acid anions, hexahalometalloidic acid anions, tetrahaloboric acid anions,

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tetrakis (perfluoroaryl) boric acid anions and tetrakisperfluoroalkylsulfonatoboric acid anions, the method comprising the steps of:

(I) mixing

(A) substituted or unsubstituted iodoarene dicarboxylates of the formula $R'_aArI(O_2CR'')_2$ wherein R' is selected from the group consisting of monovalent hydrocarbon radicals or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms, halogen atoms, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, alkoxy substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups, R" is a monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 20 carbon atoms, a has a value of from 0 to 10 and Ar denotes an arene radical having from 6 to 40 carbon atoms.

and (B) acetic acid;

(II) adding to the mixture of (I) an acid (C) in an amount such that the molar ration (A):(C) is 1:1 selected from the group consisting of perfluoroalkylsulfonic acids, hexahalometallic acids, hexahalometalloidic acids, tetrahaloboric acids, tetrakis (perfluoroaryl) boric acids and tetrakisperfluoroalkylsulfonatoboric acids at a temperature of at least -20°C. to form a homogenous reaction mixture;

(III) reacting with the homogenous reaction mixture of (II) a compound (D) selected from the group consisting of benzene, alkyl substituted benzenes, aryl substituted benzenes, arylalkyl substituted benzenes, aryloxy substituted benzenes, alkoxy substituted benzenes, arylalkoxy substituted benzenes and halobenzenes for at least 30 minutes; and

(IV) stripping off solvent from the mixture of (III).

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

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Invention Title: IMPROVED METHOD FOR THE PREPARATION OF IODONIUM SALTS

The following statement is a full description of this invention, including the best method of performing it known to us :-

IMPROVED METHOD FOR THE PREPARATION OF IODONIUM SALTS

The present invention introduces a method for the preparation of iodonium salts and/or for the production of symmetric or asymmetric diaryliodonium triflate (trifluoromethane sulfonate) salts. The diaryliodonium salts of this invention are useful as photoacid catalysts for use in acid-sensitive polymerization and in curing systems, such as radiation curable release coating compositions.

Iodonium salts and methods for their preparation have been described in the art. For example, the patented art is represented by: U.S. Patent Nos. 4,108,747; 4,125,555; 4,310,469; 4,399,071; 4,786,441; 5,066,795 and DE 4142327. The prior art in journal form includes the following: Dektar and Hacker, Journal of Organic Chemistry, 55, 639-647 (1990) discuss the photochemistry of diaryliodonium salts. Specifically, the photochemistry of diphenyl- and bis(4-methylphenyl) iodonium salts was investigated by product analysis, measurement of acid and determination of the consumption of the iodonium salts. The similarities and differences between diaryliodonium and triarylsulfonium photochemistry are also described.

Kitamura et al., Synthesis, 945-946, (1992), disclose a reagent prepared from iodosylbenzene and trifluoromethanesulfonic acid which reacts with aromatic compounds to give diaryliodonium triflates in good yields. The high reactivity of this reagent is also disclosed. In this method, a mixture of iodosobenzene and trifluoromethane sulfonic acid is made at 0°C. and is then further contacted with the desired aromatic substrate. However, iodosobenzene can only be prepared by hydrolysis of iodobenzenediacetate. In sharp contrast, the method of our invention is easier to practice and employs readily available starting materials. Furthermore, our method treats iodoarenedicarboxylates with strong acids such as trifluoromethanesulfonic acid which leads to the formation of bonded dimers. However, these dimers unexpectedly react to form the desired monomeric products. However, none of the above described references disclose the unique method of preparing diaryliodonium salts of the instant invention.

The present invention provides a method of making diaryliodonium trifluoromethane sulfonate salts which comprises contacting a mixture of iodoaryldicarboxylate with a molar equivalent of trifluormethanesulfonic acid in a non-aromatic solvent to form a homogeneous solution at temperatures of below 0°C. to 100°C., depending on the liquid range of the solvent and mixtures. The instant invention further comprises contacting the homogenous solution prepared above with a molar equivalent of a molecule containing at least one aromatic nucleus, being at most pentasubstituted (having at least one unsubstituted hydrogen attached to the aromatic nucleus), at temperatures of below 0°C. to 100°C. depending on the liquid range of the solvent and mixtures. The pure products are isolated by removing the reaction solvent and by adding a non-solvent to the residue and then triturating until solidification occurs.

The compounds prepared by this method are suitable for use with polymerizable or curable compounds such as vinyl ether functional siloxane polymers; vinyl functional siloxanes; organic vinyl ethers and olefins to afford radiation curable compositions.

It is an object of this invention to provide a method for preparing diaryliodonium salts which results in improved yields while avoiding stringent reactant requirements and reaction conditions.

It is also an object of this invention to provide such a method which is easier to practice and employs readily available starting materials.

The present invention introduces a method for the preparation of iodonium salts, the method comprising the steps of: (I) mixing (A) substituted or unsubstituted iodoarene dicarboxylates and (B) a solvent selected from the group consisting of acetic acid, chlorinated hydrocarbons and polar aprotic solvents, (II) adding to the mixture of (I) and acid (C) selected from the group consisting of perfluoroalkylsulfonic acids, hexahalometallic acids, hexahalometalloidic acids, tetrahaloboric acids, tetrakis(perfluoroaryl)boric acids and tetrakisperfluoroalkylsulfonatoboric acids at a temperature of at lease -20°C. to form a homogenous reaction mixture; (III) reacting with the homogenous reaction mixture of (II) a compound (D) selected from the group consisting of benzene, alkyl substituted benzenes, aryl substituted benzenes, arylalkyl substituted benzenes, aryloxy substituted benzenes, alkoxy substituted benzenes, arylalkoxy substituted benzenes and halobenzenes for at least 30 minutes; and (IV) stripping off solvent from the mixture of (III).

Compound (A) is a substituted or unsubstituted iodoarene dicarboxylate which is a compound having the general formula $R'_aArI(O_2CR'')_2$. R' is selected from the group consisting of monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation and having from 1 to 40 carbon atoms, halogens, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups and alkoxy substituted groups. R" is a monovalent hydrocarbon or halohydrocarbon radical free of aliphatic unsaturation and having from 1 to 20 carbon atoms, a has a value of from 0 to 5 and Ar is an arene radical having from 6 to 40 carbon atoms.

The group R' is further defined as a monovalent hydrocarbon or halohydrocarbon radical free of aliphatic unsaturation having from 1 to 40 carbon atoms. Monovalent hydrocarbon radicals free of aliphatic unsaturation which are suitable as R' include alkyl radicals such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl; cycloaliphatic radicals such as cyclohexyl; aryl radicals such as phenyl, tolyl and xylyl; and arylalkyl radicals such as benzyl or phenylethyl.

Monovalent hydrocarbon radicals also suitable as R' include arene radicals having from 6 to 40 carbon atoms such as naphthyl ($C_{10}H_7$), anthracenyl or phenanthracenyl ($C_{14}H_9$), pyrenyl ($C_{16}H_9$), napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl or 3,4-benzophenanthrenyl ($C_{18}H_{11}$), 3,4-benzopyrene or perylenyl ($C_{20}H_{11}$), 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1,2,6,7-dibenzoanthracenyl, 1,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-dibenzophenanthracenyl, pentacenyl or picenyl ($C_{22}H_{13}$), coronenyl ($C_{24}H_{11}$), 1,2,4,5-dibenzopyrene ($C_{24}H_{13}$) and hexacenyl ($C_{26}H_{15}$). Arene radicals having up to 40 carbon atoms which are suitable as R' also include combinations of the above radicals attached to one another such as phenylhexadecenyl ($C_{32}H_{19}$) or anthracenylhexacenyl ($C_{40}H_{23}$).

The group R' may also be a halogen atom or a radical selected from NO_2, CN, COOH and SO_3H. Suitable halogen atoms are fluorine, chlorine and bromine. Alkoxy groups suitable as R′ include methoxy, ethoxy, propoxy and butoxy radicals. The alkoxy substituted groups suitable as R′ include groups such as $4\text{-}CH_3O\text{-}C_6H_4$, $4\text{-}C_2H_5O\text{-}C_6H_4$, $2\text{-}CH_3O\text{-}C_6H_4$ and $2\text{-}C_2H_5O\text{-}C_6H_4$. Suitable nitro substituted groups are groups such as $3\text{-}O_2N\text{-}C_6H_4$ or $4\text{-}Cl\text{-}3\text{-}O_2N\text{-}C_6H_3$. Nitrile substituted groups suitable as R′ include groups such as $4\text{-}NC\text{-}C_6H_4$, $1\text{-}NC\text{-}C_{10}H_7$ or $2\text{-}NC\text{-}C_{10}H_7$. Suitable carboxylic acid substituted groups are exemplified by $4\text{-}HOOC\text{-}C_6H_4$ or $3\text{-}HOOC\text{-}C_6H_4$. Sulfonic acid substituted groups suitable as R′ are $4\text{-}HO_3S\text{-}C_6H_4$ or $3\text{-}HO_3S\text{-}C_6H_4$.

The group R" is further defined as a monovalent hydrocarbon or halohydrocarbon radical free of aliphatic unsaturation having from 1 to 20 carbon atoms. Monovalent hydrocarbon radicals free of aliphatic unsaturation which are suitable as R" include alkyl radicals such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl; cycloaliphatic radicals such as cyclohexyl; aryl radicals such as phenyl, tolyl and xylyl; and arylalkyl radicals such as benzyl and phenylethyl.

Ar in the formula for compound (A) denotes an aromatic radical having the formula $C_nH_{n/(2+2)}$ or of formula $C_mH_{m/(2+1)}$, wherein n has a value of 6, 10, 14, 18, 22, 26, 30, 34 or 38 and m has a value of 16, 20, 24, 28, 32, 36 or 40. Ar more specifically denotes arene radicals having from 6 to 40 carbon atoms. Suitable arene radicals are exemplified by phenyl (C_6H_5), naphthyl ($C_{10}H_7$), anthracenyl or phenanthracenyl ($C_{14}H_9$), pyrenyl ($C_{16}H_9$), napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl or 3,4-benzophenanthrenyl ($C_{18}H_{11}$), 3,4-benzopyrene or perylenyl ($C_{20}H_{11}$), 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1,2,6,7-dibenzoanthracenyl, 1,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-

dibenzophenanthracenyl, pentacenyl or picenyl ($C_{22}H_{13}$), coronenyl ($C_{24}H_{11}$), 1,2,4,5-dibenzopyrene ($C_{24}H_{13}$), hexacenyl ($C_{26}H_{15}$) and combinations of these radicals attached to one another such as phenylhexadecenyl ($C_{32}H_{19}$) or anthracenylhexacenyl ($C_{40}H_{23}$).

In step (I), compound (A) is mixed with compound (B) which is a solvent selected from the group consisting of acetic acid, chlorinated hydrocarbons and polar aprotic solvents. The chlorinated hydrocarbons are preferably selected from the group consisting of methylene chloride, chloroform and 1,2-dichloroethane. Preferably, the polar aprotic solvents are selected from the group consisting of acetonitrile, dimethylsulfoxide and benzonitrile.

For this invention from 40 to 100 percent by weight of solvent (B) can be used and it is preferred that from 90 to 100 percent by weight of (B) be employed, said percent being based on the total weight of Components (A), (C) and (CD).

Step (II) of the present invention comprises adding to the mixture of (I) an acid (C) selected from the group consisting of perfluoroalkylsulfonic acids, hexahalometallic acids, hexahalometalloidic acids, tetrahaloboric acids, tetrakis(perfluoroaryl)boric acids and tetrakisperfluoroalkylsulfonatoboric acids at a temperature of at least -20°C. to form a homogenous reaction mixture. Perfluoroalkylsulfonic acids are exemplified by perfluorobutanesulfonic acid, perfluoroethanesulfonic acid, perfluorooctanesulfonic acid or trifluoromethanesulfonic acid. Hexahalometallic acids include acids such as $HSbF_6$, $HAsF_6$, $HSbCl_6$ and $HAsCl_6$, hexahalometalloidic acids include acids such as HPF_6 and $HPCl_6$, tetrahaloboric acids include acids such as HBF_4, $HBCl_4$ and $HBBr_4$, tetrakis perfluororoaryl boric acids are exemplified by $HB(C_6H_5)_4$ and $HB(C_{10}F_7)_4$; and tetrakisperfluoroalkylsulfonatoboric acids include acids such as $HB(O_3SCF_3)_4$, $HB(O_3SC_2F5)_4$ and $HB(O_3SC_4F_9)_4$. Preferably (C) is selected from the group consisting of trifluoromethanesulfonic acid, perfluorobutylsulfonic acid, hexafluoroantimonic acid, hexafluorophosphoric acid, hexafluoroarsenic acid, tetrafluoroboric acid, tetrakis(pentafluorophenyl)boric acid and tetrakis(trifluoromethanesulfanato)boric acid.

Step (III) in the present invention comprises reacting with the homogeneous reaction mixture of (II) a compound (D) selected from the group consisting of benzene, alkyl substituted benzenes, aryl substituted benzenes, arylalkyl substituted benzenes, alkoxy substituted benzenes, arylalkoxy substituted benzenes and halobenzenes for at least 30 minutes. Preferably, compound (D) is selected from the group consisting of benzene, toluene, xylene, butylbenzene, t-butylbenzene, dodecylbenzene, tetracosyl benzene, octylbenzene, 1-phenyl-5-methylheptane, bisdodecylbenzene, fluorobenzene, anisole, octyloxybenzene, dodecyloxybenzene, octadecyloxybenzene and 1-phenoxy-5-methylheptane.

Step (IV) of the present invention comprises stripping off solvent from the mixture of (III). Methods of stripping volatile components are well known in the art and need no extensive delineation herein. Any method of removing volatile components can be used in this invention, such as distillation; evaporation; by the passage of steam; air; or other gas through the liquid mixture; molecular stills; rotoevaporators and wiped film evaporators. The preferred method of stripping the solvent from the mixture of step (III) is by employing a rotoevaporator.

It is preferred for the present invention that the molar ratio of (A) to (C) to (D) is 0.95 - 1.05 to 0.95 - 1.05 to 0.95 - 1.05. It is preferred for purposes of the instant invention that the molar ratio of (A) to (C) to (D) is 1 to 1 to 1.

The method of the present invention can further comprise the step of adding a mixture of an organic solvent and water prior to step (IV) which results in the formation of an organic layer and an aqueous layer. Suitable organic solvents include methylene chloride, acetonitrile, mineral spirits and chlorinated hydrocarbons; benzene; toluene; ethers and xylene. Preferred organic solvents are toluene and diethyl ether. The mixture of organic solvent and water can be added in a ratio of 99 weight percent organic solvent to 1 weight percent of water to a ratio of 1 weight percent organic solvent to 99 weight percent of water. It is preferred that the organic solvent make up at least 30 weight percent of this mixture. Addition of this mixture results in the formation of two layers, an organic layer and an aqueous layer. Separation of the organic layer and the aqueous layer comprises allowing the non-miscible layers to phase separate and then drawing the less dense layer off the top and the more dense layer off the bottom of a separation vessel. The manner in which the two layers are mechanically separated is not critical as long as the two layers are isolated. Separation of the two layers may be accomplished by any of the separation methods well known to those skilled in the art. Thus, separation may be accomplished by evaporation, distillation, drying, gas absorption, sedimentation, solvent extraction, press extraction, adsorption and filtration.

Our method can further comprise adding water to the separated organic layer. The amount of water added to the organic layer is not critical and may be readily determined through routine experimentation by those of ordinary skill in the art. This can then be followed by stripping of the organic layer. Methods of stripping the organic layer are as delineated above.

The present invention can further comprise heating the mixture after step (III). The mixture in this method is preferably heated at a temperature of 20°C. to 100°C. It is highly preferred that the mixture be heated at a temperature of from 40 to 70°C. after step (III).

The diaryliodonium salts prepared by our invention are diaryliodonium salts having the general formula $R^{i}_{a}ArI^{+}ArR^{ii}_{b}X^{-}$. R^{i} is selected from the group consisting of monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms, halogen atoms, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups and alkoxy substituted groups; R^{ii} is selected from the group consisting of hydrogen, monovalent hydrocarbon radicals free of aliphatic unsaturation and having from 1 to 40 carbon atoms, alkoxy radicals, arylalkoxy radicals, aryloxy radicals and halogen atoms; Ar denotes arene radicals having from 6 to 40 carbon atoms, a has a value of from 0 to 10, b has value of from 0 to 10 and X^{-} is an anion selected from the group consisting of perfluoroalkylsulfonic acid anions, hexahalometallic acid anions, hexahalometalloidic acid anions, tetrahaloboric acid anions, tetrakis(perfluoroaryl)boric acid anions and tetrakisperfluoroalkylsulfonatoboric acid anions.

More specifically, Ar denotes an aromatic radical having the formula $C_nH_{n/(2+2)}$ or of formula $C_mH_{m/(2+1)}$, wherein n has a value of 6, 10, 14, 18, 22, 26, 30, 34 or 38 and m has a value of 16, 20, 24, 28, 32, 36 or 40.

The group R^i is monovalent hydrocarbon or halohydrocarbon radical free of aliphatic unsaturation having from 1 to 40 carbon atoms. Suitable monovalent hydrocarbon radicals free of aliphatic unsaturation include alkyl radicals such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl; cycloaliphatic radicals such as cyclohexyl; aryl radicals such as phenyl, tolyl and xylyl; and arylalkyl radicals such as benzyl, phenylmethyl, phenylethyl and phenylnaphthyl.

Monovalent hydrocarbon radicals also suitable as R^i include arene radicals having from 6 to 40 carbon atoms such as naphthyl ($C_{10}H_7$), anthracenyl or phenanthracenyl ($C_{14}H_9$), pyrenyl ($C_{16}H_9$), napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl or 3,4-benzophenanthrenyl ($C_{18}H_{11}$), 3,4-benzanthracenyl or 3,4-benzophenanthrenyl ($C_{18}H_{11}$), 3,4-benzopyrene or perylenyl ($C_{20}H_{11}$), 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1,2,6,7-dibenzoanthracenyl, 1,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-dibenzophenanthracenyl, pentacenyl or picenyl ($C_{22}H_{13}$), coronenyl ($C_{24}H_{11}$), 1,2,4,5-dibenzopyrene ($C_{24}H_{13}$) and hexacenyl ($C_{26}H_{15}$). Arene radicals having up to 40 carbon atoms which are suitable as R^i also include combinations of the above radicals attached to one another such as phenylhexadecenyl ($C_{32}H_{19}$) or anthracenylhexacenyl ($C_{40}H_{23}$).

The group R^i may also be a halogen atom or a radical selected from NO_2, CN, COOH and SO_3H. Halogen atoms which are suitable include fluorine, chlorine and bromine. Suitable alkoxy groups include radicals such as methoxy, ethoxy, propoxy and butoxy. Nitro substituted groups suitable as R^i include groups such as $3\text{-}O_2N\text{-}C_6H_4$ or $4\text{-}Cl\text{-}3\text{-}O_2N\text{-}C_6H_3$. Nitrile substituted groups suitable are exemplified by groups such as $4\text{-}NC\text{-}C_6H_4$, $1\text{-}NC\text{-}C_{10}H_7$ or $2\text{-}NC\text{-}C_{10}H_7$. Suitable carboxylic acid substituted groups are groups such as $4\text{-}HOOC\text{-}C_6H_4$ or $3\text{-}HOOC\text{-}C_6H_4$. Sulfonic acid substituted groups suitable as R^i are $4\text{-}HO_3S\text{-}C_6H_4$ or $3\text{-}HO_3S\text{-}C_6H_4$. The alkoxy substituted groups suitable as R^i are $4\text{-}CH_3O\text{-}C_6H_4$, $4\text{-}C_2H_5O\text{-}C_6H_4$, $2\text{-}CH_3O\text{-}C_6H_4$ and $2\text{-}C_2H_5O\text{-}C_6H_4$.

The monovalent hydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms (including arene radicals having from 6 to 40 carbon atoms), alkoxy substituted groups and halogen atoms suitable as R^{ii} are as delineated above for R^i including preferred embodiments thereof. Suitable arylalkoxy radicals include benzyloxy and phenylethyloxy. Aryloxy radicals suitable as R^{ii} are exemplified by phenoxy and napthoxy.

Ar denotes arene radicals having from 6 to 40 carbon atoms. Arene radicals suitable as Ar are phenyl (C_6H_5), naphthyl ($C_{10}H_7$), anthracenyl or phenanthracenyl ($C_{14}H_9$), pyrenyl ($C_{16}H_9$), napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl or 3,4-benzophenanthrenyl ($C_{18}H_{11}$), 3,4-benzopyrene or perylenyl ($C_{20}H_{11}$), 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1,2,6,7-dibenzoanthracenyl, 1,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-dibenzophenanthracenyl, pentacenyl or picenyl ($C_{22}H_{13}$), coronenyl ($C_{24}H_{11}$), 1,2,4,5-dibenzopyrene ($C_{24}H_{13}$), hexacenyl ($C_{26}H_{15}$) and combinations of these radicals attached to one another such as phenylhexadecenyl ($C_{32}H_{19}$) or anthracenylhexacenyl ($C_{40}H_{23}$).

The anion X^- is selected from the group consisting of perfluoroalkylsulfonic acid anions, hexahalometallic acid anions, hexahalometalloidic acid anions, tetrahaloboric acid anions, tetrakis(perfluoroaryl)boric acid anions and tetrakisperfluoroalkylsulfonatoboric acid anions. Perfluoroalkylsulfonic acid anions are exemplified by perfluorobutanesulfonic acid anions, perfluoroethanesulfonic acid anions, perfluoro-octanesulfonic acid anions or trifluoromethanesulfonic acid anions. Hexahalometallic acid anions include anions such as SbF_6^-, AsF_6^-, $SbCl_6^-$ and $AsCl_6^-$, hexahalometalloidic acid anions include anions such as PF_6^- and PCl_6^-, tetrahaloboric acid anions include anions such as BF_4^-, BCl_4^- and BBr_4^-, tetrakis perfluoroaryl boric acid anions are exemplified by $HB(C_6F_5)_4^-$ and $B(C_{10}F_7)_4^-$ and tetrakisperfluoroalkylsulfonatoboric acid anions include anions such as $B(O_3SCF_3)_4^-$, $B(O_3SC_2F_5)_4^-$ and $B(O_3SC_4F_9)_4^-$. It is preferred that X^- is trifluoromethanesulfonate.

The following examples are disclosed to further teach the invention which is delineated by the appended claims. All amounts (parts and percentages) are by weight unless otherwise indicated.

Example 1

To a stirred suspension of 6.44 g (grams) (0.02 mole) of iodobenzene diacetate (from Aldrich, Madison, WI) in 20 ml of glacial acetic acid (solvent from FISHER SCIENTIFIC, Pittsburg, PA) were added 3.0 g (0.02 mole) trifluoromethanesulfonic acid (triflic acid, TfOH or HOTf).

(FC-24^{TM} from 3M Co., Minneapolis, MN) in dropwise fashion while the solution was at ambient temperature. After all solids were completely dissolved and a clear yellow solution was obtained, there was added to this stirred yellow solution 2.12 g of 1,3-xylene (Ar from Aldrich) in a dropwise fashion, also while the solution was at ambient temperature. The resulting mixture was allowed to stir for 30 minutes. After this time the solvent was removed by evaporation on a rotary evaporator under an ultimate pressure of less than 133 Pa (1 mm Hg) and at a bath temperature of less than 80°C. An oily residue was obtained. The residue was triturated with diethylether (crystallizing solvent) until it solidified, after which it was collected by filtration and washed with more diethyl ether and dried in vacuo. The product was collected in a crystalline form and had a 94% of theoretical yield.

Example 2

To a stirred suspension of 6.44 g (0.02 mole) iodobenzene diacetate (Aldrich, Madison, WI) in 20 ml glacial acetic acid (solvent from FISHER SCIENTIFIC) were added 3.0 g (0.02 mole) trifluoromethanesulfonic acid (FC-24^{TM} from 3M Co) in dropwise fashion while the solution was at ambient temperature. After all solids were completely dissolved and a clear yellow solution was obtained, there was added to this stirred yellow solution 4.92 g of dodecylbenzene (Ar from Johnson Matthey Catalog Co., Ward Hill, MA) in a dropwise fashion while the solution was at ambient temperature. The resulting mixture was allowed to stir for 3 hours. Acetic acid was then removed in a rotary evaporator leaving a reaction mixture of oil and acetic acid. After this time, there was added to the reaction mixture 30 ml of toluene (from FISHER) and 30 ml deionized water and the resulting aqueous and organic layers were separated. The organic layer was subsequently repeatedly washed with further portions of deionized water until the pH of the separated water layer was greater than 5. The toluene solvent and residual water was then removed from the separated organic layer by evaporation on a rotary evaporator under an ultimate pressure of less than 133 Pa (1 mm Hg) and at a bath temperature of less than 80°C. The product was a residue from this separation process in the form of a viscous liquid oil. The oil was converted to a low-melting solid product, in the case of dodecylbenzene as the substrate, by dissolving the viscous oil in toluene and then adding the solution to an excess of n-pentane and recovering the precipitated solids formed thereby by means of filtration, washing the precipitate with more clean pentane and then drying in vacuo. However, the viscous oil was a perfectly suitable form of the intended product.

Example 3

To a stirred suspension of 6.44 g (0.02 mole) iodobenzene diacetate (Aldrich) in 20 ml glacial acetic acid (solvent from FISHER SCIENTIFIC) were added 3.0 g (0.02 mole) trifluoromethanesulfonic acid (FC-24^{TM} from 3M Co.) in dropwise fashion while the solution was at ambient temperature. After all solids were completely dissolved and a clear yellow solution was obtained, there was added to this stirred yellow solution 4.92 g of dodecylbenzene (Ar from Johnson Matthey) in a dropwise fashion while the solution was at ambient temperature. The resulting mixture was allowed to stir for 3 hours. Acetic acid was then removed in a rotary evaporator leaving a reaction mixture of oil and acetic acid. After this time, there was added to the reaction mixture 30 ml of toluene (from FISHER) and 30 ml deionized water and this mixture was agitated to allow the acetic acid to mix with the water phase. The water phase was then drawn off the top and more fresh water was added. The procedure was repeated several times until acetic acid could not be detected in the water phase. The toluene solvent and residual water were then removed from the separated organic layer by evaporation on a rotary evaporator under an ultimate pressure of less than 133 Pa (1 mm Hg) and at a bath temperature of less than 80°C. The product was a residue from this separation process in the form of a viscous liquid oil at stripping temperatures but was a solid waxy substance at room temperature. The solid was further purified, in the case of dodecylbenzene as the substrate, by dissolving the solid product in toluene and then adding this solution to an excess of n-pentane and recovering the precipitated solids formed thereby by means of filtration, washing the precipitate with more clean pentane and then drying in vacuo.

Examples 4-45

In the examples below, the above procedure was utilized. Table I delineates the amount of iodobenzene diacetate, solvent type, solvent amount, amount of trifluoromethanesulfonic acid (FC-24^{TM}), aromatic compound and amount of Ar. Mixing times ranged from an hour to several hours and mixing temperatures were at room temperature or ranged from 45 to 70°C. Where a crystallizing solvent was employed, the procedure of Example 1 was also followed. Where no crystallizing solvent was used, the procedure of Example 2 was employed. When the oil is reported as being in the form of a solid then the procedure of Example 3 was followed. Table II describes the amount of oil produced (product), oil color, crystallizing solvent (if used), product obtained and the percent of theoretical yield obtained. In these examples, triflate denotes trifluoromethanesulfonate. The identity of the obtained product was determined by NMR (Nuclear Magnetic Resonance) and IR (Infrared Spectroscopy).

TABLE I

	Iodobenzene Diacetate (g)	Solvent	Solvent (ml)	FC-24 (g)	Ar	Ar(g)
Ex.4	9.66	HOAc	20	4.51	benzene	2.35
5	6.44	HOAc	20	3.00	benzene	1.56
6	3.24	HOAc	20	1.48	toluene	0.91
7	3.22	HOAc	20	1.51	m-xylene	1.07
8	3.29	HOAc	20	1.52	pentamethylbenzene	1.49
9	6.44	HOAc	20	3.00	n-butylbenzene	2.68
10	3.23	HOAc	20	1.50	sec-butylbenzene	1.37
11	3.25	HOAc	20	1.50	tert-butylbenzene	1.34
12	3.24	HOAc	20	1.51	phenylcyclohexane	1.60
13	6.47	HOAc	20	3.02	1-phenylhexane	3.26
14	9.69	HOAc	20	4.52	dodecylbenzene	7.40
15	6.43	HOAc	20	3.00	dodecylbenzene	4.94
16	9.67	HOAc	20	4.50	dodecylbenzene	7.39
17	9.68	HOAc	20	4.50	dodecylbenzene	7.40
18	9.72	HOAc	20	4.53	dodecylbenzene	7.42
19	9.66	HOAc	20	4.52	dodecylbenzene	7.40
20	9.68	CH2Cl2	20	4.52	dodecylbenzene	7.41
21	6.46	HOAc	20	3.00	dodecylbenzene	4.93
* 22	6.75	HOAc	20	3.15	1-phenyldodecane	5.17
23	6.76	HOAc	20	3.02	benzene	1.56
24	6.44	HOAc	20	3.01	fluorobenzene	1.93
25	9.68	HOAc	20	4.51	chlorobenzene	3.38
26	6.44	HOAc	20	3.02	iodobenzene	4.10
27	6.44	HOAc	20	3.02	3-iodotoluene	4.37
28	3.23	HOAc	25	1.49	methylphenylether	1.01
29	3.22	CH3CN	25	1.48	methylphenylether	1.10
30	3.24	CH2Cl2	25	1.51	methylphenylether	1.11
31	3.24	HOAc	20	1.51	methylphenylether	1.09
32	3.22	CH2Cl2	25	1.51	methylphenylether	1.13
33	3.22	CH3CN	25	1.50	methylphenylether	1.10
34	3.22	HOAc	20	1.51	butylphenylether	1.50
35	12.88	HOAc	50	6.47	octylphenylether	8.65
36	3.24	HOAc	20	1.50	octadecylphenylether	3.46
37	6.44	HOAc	20	3.01	4-phenoxybutyl bromide	4.58
38	6.43	CH2Cl2	20	3.00	2-phenoxyethanol	2.77
39	6.45	HOAc	20	3.00	2-phenoxyethanol	2.76
40	6.46	CH2Cl2	20	3.00	2-phenoxyethanol	2.77
41	12.89	HOAc	20	6.01	2-phenoxyethanol	5.54
42	12.86	HOAc	50	6.00	2-phenoxyethanol	5.53
43	6.46	HOAc	20	3.02	thiophene	1.68
44	9.73	HOAc	20	4.52	dodecylbenzene	7.41
45	10.08	HOAc	20	4.50	dodecylbenzene	7.39

* - 3-Iodotoluene Diacetate was substituted for Iodobenzene Diacetate

Table II

Ex.	Oil(g)	Oil Color	Crystallizing Solvent	%Yield	Product Obtained
4	10.80	orange	ether	59.5	Diphenyliodonium triflate
5	8.69	yellow	ether	50.0	Diphenyliodonium triflate
6	4.92	yellow	ether	51.6	4-methylphenylphenyl iodonium triflate
7	5.35	white	ether	93.3	dimethylphenylphenyl iodonium triflate
8	4.44	dark purple	ether	23.5	pentamethylphenylphenyl iodonium triflate
9	10.45	brown	ether	58.4	butylphenylphenyl iodonium triflate
10	5.72	yellow	ether	58.2	s-butylphenylphenyl iodonium triflate
11	5.49	yellow	ether	45.8	t-butylphenylphenyl iodonium triflate
12	6.15	yellow	ether	51.6	cyclohexylphenylphenyl iodonium triflate
13	10.68	brown	none	73.8	hexylphenylphenyl iodonium triflate
14	20.01	yellow	none	80.6	dodecylphenylphenyl iodonium triflate
15	12.57	brown	none	80.2	dodecylphenylphenyl iodonium triflate
16	18.61	brown	none	79.2	dodecylphenylphenyl iodonium triflate
17	20.10	yellow	none	78.8	dodecylphenylphenyl iodonium triflate
18	19.45	yellow	none	78.6	dodecylphenylphenyl iodonium triflate
19	18.97	orange	none	72.0	dodecylphenylphenyl iodonium triflate
20	18.61	orange	none	69.0	dodecylphenylphenyl iodonium triflate
21	12.30	orange	none	47.5	dodecylphenylphenyl iodonium triflate
22	12.08	brown	none	76.3	dodecylphenylphenyl iodonium triflate
23	8.32	yellow-orange	ether	53.2	3-methylphenylphenyl iodonium triflate
24	8.86	orange	ether	68.8	4-fluorophenylphenyl iodonium triflate
25	13.27	orange	ether	40.2	4-chlorophenylphenyl iodonium triflate

Ex.	Oil(g)	Oil Color	Crystallizing Solvent	%Yield	Product Obtained
26	8.66	orange	ether	52.8	4-iodophenylphenyl iodonium triflate
27	10.96	orange	ether	50.9	iodotolylphenyl iodonium triflate
28	4.15	red-brown	CH2Cl2-ether	56.3	methoxyphenylphenyl iodonium triflate
29	3.19	brown	ether	54.5	methoxyphenylphenyl iodonium triflate
30	3.39	brown	ether	53.5	methoxyphenylphenyl iodonium triflate
31	5.75	dark brown	ether	50.9	methoxyphenylphenyl iodonium triflate
32	2.37	red-brown	CH2Cl2-ether	21.7	methoxyphenylphenyl iodonium triflate
33	1.79	red-brown	CH2Cl2-ether	15.4	methoxyphenylphenyl iodonium triflate
34	5.14	black-green	ether	61.1	butyloxyphenylphenyl iodonium triflate
35	18.98	brown	none	67.0	octyloxyphenylphenyl iodonium triflate
36	12.79	dark brown	ether	73.0	3bromopropoxyphenylphenyl iodonium triflate
37	11.93	brown	ether	82.6	4-(4'-bromobutoxy) phenylphenyl iodonium triflate
38	10.88	brown	ether	71.8	4-(2-hydroxyethoxy) phenylphenyl iodonium triflate
39	11.42	dark brown	ether	71.3	4-(2-hydroxyethoxy) phenylphenyl iodonium triflate
40	13.45	brown	ether	71.3	4-(2-hydroxyethoxy) phenylphenyl iodonium triflate
41	20.40	brown	ether	58.3	4-(2-hydroxyethoxy) phenylphenyl iodonium triflate
42	20.97	brown	ether	7.1	4-(2-hydroxyethoxy) phenylphenyl iodonium triflate
43	10.35	dark blue	ether	8.2	2-thiophenylphenyl iodonium triflate
44	solid	yellow	none	93.0	Dodecylphenyphenyl iodonium triflate
45	solid	yellow	none	94.8	(Dodecylphenyl) (3-methylphenyl) iodonium triflate

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for the preparation of iodonium salts of the formula $R^{i}_{a}ArI^{+}$ $ArR^{ii}_{bx}{}^{-}$ where R^{i} is selected from the group consisting of monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms, halogen atoms, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups and alkoxy substituted groups. R^{ii} is selected from the group consisting of hydrogen, monovalent hydrocarbon radicals free of aliphatic unsaturation and having from 1 to 40 carbon atoms, alkoxy radicals, arylalkoxy radicals, aryloxy radicals and halogen atoms, Ar denotes arene radicals having from 6 to 40 carbon atoms, a has a value of from 0 to 10, b has value of from 0 to 10 and X^{-} is an anion selected from the group consisting of perfluoroalkylsulfonic acid anions, hexahalometallic acid anions, hexahalometalloidic acid anions, tetrahaloboric acid anions, tetrakis (perfluoroaryl) boric acid anions and tetrakisperfluoroalkylsulfonatoboric acid anions, the method comprising the steps of:

(I) mixing

(A) substituted or unsubstituted iodoarene dicarboxylates of the formula $R'_{a}ArI(O_2CR'')_2$ wherein R' is selected from the group consisting of monovalent hydrocarbon radicals or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 40 carbon atoms, halogen atoms, NO_2, CN, COOH, SO_3H, alkoxy groups, nitro substituted groups, nitrile substituted groups, alkoxy substituted groups, carboxylic acid substituted groups, sulfonic acid substituted groups, R" is a monovalent hydrocarbon or halohydrocarbon radicals free of aliphatic unsaturation having from 1 to 20 carbon atoms, a has a value of from 0 to 10 and Ar denotes an arene radical having from 6 to 40 carbon atoms.

and (B) acetic acid;

(II) adding to the mixture of (I) an acid (C) in an amount such that the molar ration (A):(C) is 1:1 selected from the group consisting of perfluoroalkylsulfonic acids, hexahalometallic acids, hexahalometalloidic acids, tetrahaloboric acids, tetrakis (perfluoroaryl) boric acids and tetrakisperfluoroalkylsulfonatoboric acids at a temperature of at least -20°C. to form a homogenous reaction mixture;

(III) reacting with the homogenous reaction mixture of (II) a compound (D) selected from the group consisting of benzene, alkyl substituted benzenes, aryl substituted benzenes, arylalkyl substituted benzenes, aryloxy substituted benzenes, alkoxy substituted benzenes, arylalkoxy substituted benzenes and halobenzenes for at least 30 minutes; and

(IV) stripping off solvent from the mixture of (III).

2. A method according to claim 1 wherein (C) id selected from the group consisting of trifluoromethanesulfonic acid, perfluorobutylsulfonic acid, hexafluoroantimonic acid, hexafluorophosphoric acid, hexafluoroarsenic acid, tetrafluoroboric acid, tetrakis(pentafluorophenyl)boric acid and tetrakis(trifluoromethanesulfanato)boric acid.

3. A method according to claim 1 wherein (D) is selected from the group consisting of benzene, toluene, xylenes, butylbenzene, t-butylbenzene, dodecylbenzene, tetracosyl benzene, octylbenzene, 1-phenyl-5-methylheptane, bisdodecylbenzene, fluorobenzene, anisole, octyloxybenzene, dodecyloxybenzene, octadecyloxybenzene and 1-phenoxy-5-methylheptane.

4. A method according to claim 1 wherein the method further comprises the step of adding a mixture of an organic solvent and water prior to step (IV) which results in the formation of an organic layer and an aqueous layer.

5. A method according to claim 4 wherein the method further comprises adding water to the organic layer.

6. A method according to claim 5 wherein the method further comprises stripping the organic layer.

7. A method according to claim 1 wherein the method further comprises heating the mixture after step (III).

8. A method according to claim 1 wherein the monovalent hydrocarbon radicals having from 1 to 40 carbon atoms are selected from the group consisting of methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, cyclohexyl, phenyl, tolyl, xylyl, benzyl, phenylmethyl, phenylethyl, phenylnaphthyl, naphthyl, anthracenyl, phenanthracenyl, pyrenyl, napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl, 3,4-benzophenanthrenyl, 3,4-benzopyrene, perylenyl, 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1,2,6,7-dibenzoanthracenyl, 1 ,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-dibenzophenanthracenyl, pentacenyl, picenyl, coronenyl, 1,2,4,5-dibenzopyrene, hexacenyl, phenylhexadecenyl and anthracenylhexacenyl.

9. A method according to claim 1 wherein the arene radical is selected from the group consisting of phenyl, naphthyl, anthracenyl, phenanthracenyl, pyrenyl, napthacenyl, 9,10-benzophenanthrenyl, chrysenyl, 1,2-benzanthracenyl, 3,4-benzophenanthrenyl, 3,4-benzopyrene, perylenyl, 1,2,3,4-dibenzanthracenyl, 1,2,5,6-dibenzanthracenyl, 1 ,2,6,7-dibenzoanthracenyl, 1 ,2,7,8-dibenzanthracenyl, 1,2,6,7-dibenzophenanthracenyl, 1,2,7,8-dibenzophenanthracenyl, pentacenyl, picenyl, coronenyl, 1,2,4,5-dibenzopyrene, hexacenyl, phenylhexadecenyl and anthracenylhexacenyl.

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IMPROVED METHOD FOR THE PREPARATION OF IODONIUM SALTS

ABSTRACT

The present invention relates to an improved method for the preparation of iodonium salts. More specifically, the present invention relates to an improved method for the production of symmetric or asymmetric diaryliodonium triflate (trifluoromethane sulfonate) salts. The diaryliodonium salts of the present invention are useful as photoacid catalysts for use in acid-sensitive polymerization and in curing systems such as radiation curable release coating compositions.