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CA 2912279 A1 2008/10/02

(21) 2 912 279

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2008/03/21

(41) Mise à la disp. pub./Open to Public Insp.: 2008/10/02

(62) Demande originale/Original Application: 2 857 831

(30) Priorité/Priority: 2007/03/23 (US60/896669)

(51) Cl.Int./Int.Cl. *C07C 381/00* (2006.01)

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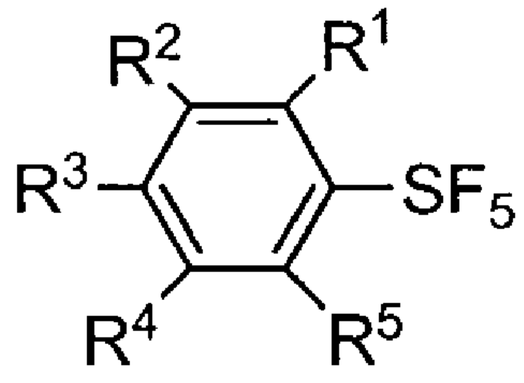
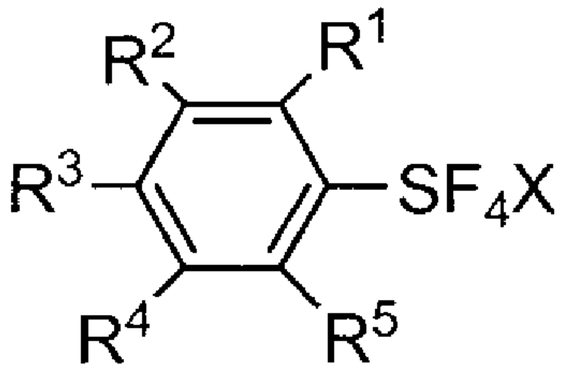
(54) Titre : PROCEDE DE PRODUCTION DE PENTAFLUORURES D'ARYLSOUFRE
(54) Title: PROCESS FOR PRODUCING ARYLSULFUR PENTAFLUORIDES



(I)

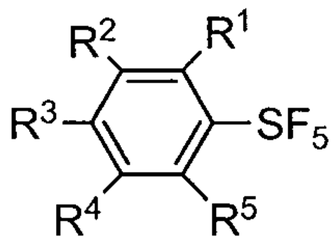


(IV)

(57) Abrégé/Abstract:
Conventional synthetic methodologies to produce arylsulfur pentafluorides have proven difficult. The invention relates to an improved process for preparing an arylsulfur pentafluoride having a formula (I): (see formula I) the process comprising: reacting an arylsulfur halotetrafluoride having a formula (IV): (see formula IV) with a fluoride source, wherein the fluoride source is a solid or liquid having a boiling point of approximately 0°C or more at 1 atm, to form the arylsulfur pentafluoride. Arylsulfur pentafluorides compounds are used to introduce one or more sulfur pentafluoride groups into various commercial organic molecules.

Abstract

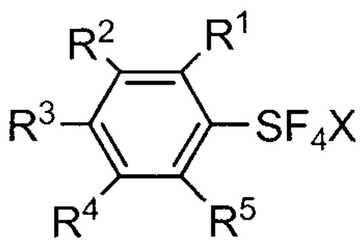
Conventional synthetic methodologies to produce arylsulfur pentafluorides have proven difficult. The invention relates to an improved process for preparing an arylsulfur pentafluoride having a formula (I):



---------- (I)

the process comprising:

reacting an arylsulfur halotetrafluoride having a formula (IV):



---------- (IV)

with a fluoride source, wherein the fluoride source is a solid or liquid having a boiling point of approximately 0°C or more at 1 atm, to form the arylsulfur pentafluoride. Arylsulfur pentafluorides compounds are used to introduce one or more sulfur pentafluoride groups into various commercial organic molecules.

PROCESS FOR PRODUCING ARYLSULFUR PENTAFLUORIDES

TECHNICAL FIELD

[0001] The invention relates to methods and compositions useful in the preparation of arylsulfur pentafluorides.

BACKGROUND OF THE INVENTION

[0002] Arylsulfur pentafluorides compounds are used to introduce one or more sulfur pentafluoride groups into various commercial organic molecules. In particular, arylsulfur pentafluorides have been shown as useful compounds (as product or intermediate) in the development of liquid crystals, in bioactive chemicals such as fungicides, herbicides, and insecticides, and in other like materials [see Fluorine-containing Synthons (ACS Symposium Series 911), ed by V. A. Soloshonok, American Chemical Society (2005), pp. 108-113]. However, as discussed herein, conventional synthetic methodologies to produce arylsulfur pentafluorides have proven difficult and are a concern within the art.

[0003] Generally, arylsulfur pentafluorides are synthesized using one of the following synthetic methods: (1) fluorination of diaryl disulfies or arylsulfur trifluoride with AgF_2 [see J. Am. Chem. Soc., Vol. 84 (1962), pp. 3064-3072, and J. Fluorine Chem. Vol. 112 (2001), pp. 287-295]; (2) fluorination of di(nitrophenyl) disulfides, nitrobenzenethiols, or nitrophenylsulfur trifluorides with molecular fluorine (F_2) [see Tetrahedron, Vol. 56 (2000), pp. 3399-3408; Eur. J. Org. Chem., Vol. 2005, pp. 3095-3100; and USP 5,741,935]; (3) fluorination of diaryl disulfides or arenethiols with F_2, CF_3OF, or $CF_2(OF)_2$ in the presence or absence of a fluoride source (see US Patent Publication No. 2004/0249209 A1); (4) fluorination of diaryl disulfides with XeF_2 [see J. Fluorine Chem., Vol. 101 (2000), pp. 279-283]; (5) reaction of 1,4-bis(acetoxy)-2-cyclohexene with SF_5Br followed by dehydrobromination or hydrolysis and then aromatization reactions [see J. Fluorine Chem., Vol. 125 (2004), pp. 549-552]; (6) reaction of 4,5-dichloro-1-cyclohexene with SF_5Cl followed by dehydrochlorination [see Organic Letters, Vol. 6 (2004), pp. 2417-2419 and PCT WO 2004/011422 A1]; and (7) reaction of SF_5Cl with acetylene, followed by bromination, dehydrobromination, and reduction with zinc, giving pentafluorosulfanylacetylene, which was then reacted with butadiene, followed by an aromatization reaction at very high temperature [see J. Org. Chem., Vol. 29 (1964), pp. 3567-3570].

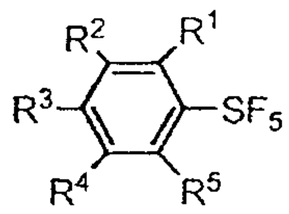
[0004] Each of the above synthetic methods has one or more drawbacks making it either impractical (time or yield), overly expensive, and/or overly dangerous to practice. For example, synthesis methods (1) and (4) provide low yields and require expensive reaction agents, e.g., AgF_2 and XeF_2. Methods (2) and (3) require the use of F_2, CF_3OF, or $CF_2(OF)_2$, each of which is toxic, explosive, and corrosive, and products produced using these methods are at a relatively low yield. Note that handling of these gasses is expensive from the standpoint of the gasses production, storage and use. In addition, synthesis methods that require the use of F_2, CF_3OF, and/or $CF_2(OF)_2$ are limited to the production of deactivated arylsulfur pentafluorides, such as nitrophenylsulfur pentafluorides, due to their extreme reactivity, which leads to side-reactions such as fluorination of the aromatic rings when not deactivated. Methods (5) and (6) also require expensive reactants, e.g., SF_5Cl or SF_5Br, and have narrow application because the starting cyclohexene derivatives are limited. Finally, method (7) requires the expensive reactant SF_5Cl and includes many reaction steps to reach the arylsulfur pentafluorides (timely and low yield). Therefore, problems with the production methods for arylsulfur pentafluorides have made it difficult to prepare the material in a safe, cost effective and timely fashion.

[0005] Phenylsulfur chlorotetrafluoride, p-methylphenylsulfur chlorotetrafluoride, and p-nitrophenylsulfur chlorotetrafluoride were detected in the reaction of diphenyl disulfide, bis(p-methylphenyl) disulfide, and bis(p-nitrophenyl) disulfide, respectively, with XeF_2 in the presence of tetraethylammonium chloride (see Can. J. Chem., Vol. 75, pp.1878-1884). Chemical structures of the chlorotetrafluoride compounds were assigned by analysis of the NMR data of the reaction mixtures, but these compounds were not isolated. Therefore, the physical properties of the chlorotetrafluorides were unknown. This synthesis method using XeF_2 was industrially impractical because XeF_2 is overly expensive for large scale production.

[0006] The present invention is directed toward overcoming one or more of the problems discussed above.

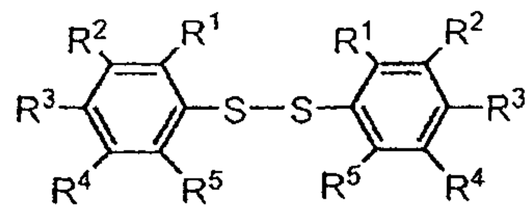
SUMMARY OF THE INVENTION

[0007] The present invention provides novel processes for the production of arylsulfur pentafluoride, as represented by formula (I):

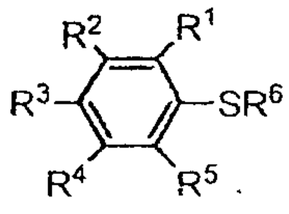


(I)

Embodiments of the invention include reacting at least one aryl sulfur compound, having a formula (IIa) or (IIb),

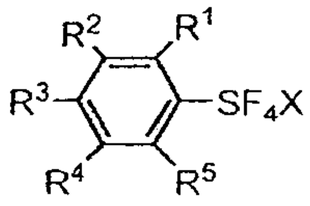


(IIa)



(IIb)

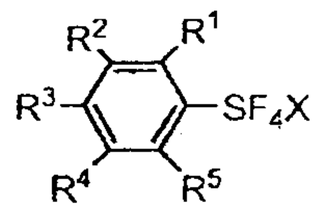
with a halogen selected from the group of chlorine, bromine, iodine and interhalogens, and a fluoro salt (M^+F^-, formula III) to form an arylsulfur halotetrafluoride having a formula (IV):



(IV)

The arylsulfur halotetrafluoride (formula IV) is reacted with a fluoride source to form the arylsulfur pentafluoride (formula I).

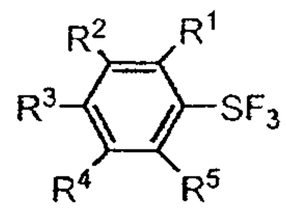
[0008] Embodiments of the present invention also provide processes for producing an arylsulfur pentafluoride (formula I) by reacting at least one aryl sulfur compound, having a formula (IIa) or (IIb), with a halogen selected from the group of chlorine, bromine, iodine and interhalogens, and a fluoro salt (M^+F^-, formula III) to form an arylsulfur halotetrafluoride having a formula (IV):



(IV)

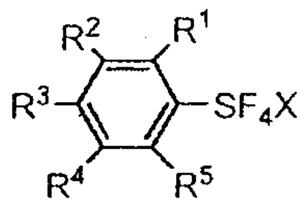
The arylsulfur halotetrafluoride (formula IV) is reacted with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the arylsulfur pentafluoride (formula I).

[0009] Embodiments of the present invention also provide processes for producing arylsulfur pentafluorides (formula I) by reacting an arylsulfur trifluoride having a formula (V):



---------- (V)

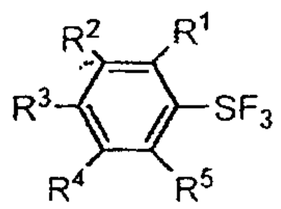
with a halogen selected from the group of chlorine, bromine, iodine and interhalogens, and a fluoro salt (formula III) to form an arylsulfur halotetrafluoride having a formula (IV):



---------- (IV)

The arylsulfur halotetrafluoride (formula IV) is reacted with a fluoride source to form the arylsulfur pentafluoride (formula I).

[0010] Embodiments of the present invention also provide processes for producing arylsulfur pentafluorides (formula I) by reacting an arylsulfur trifluoride having a formula (V):



---------- (V)

with a halogen selected from the group of chlorine, bromine, iodine and interhalogens, and a fluoro salt (formula III) to form an arylsulfur halotetrafluoride having a formula (IV).

[0011] The arylsulfur halotetrafluoride (formula IV) is reacted with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the arylsulfur pentafluoride (formula I).

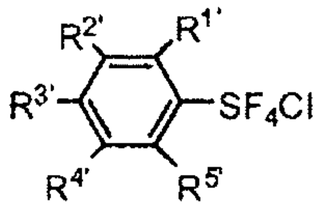
[0012] Embodiments of the present invention further provide processes for producing arylsulfur halotetrafluoride (formula IV) by reacting at least one aryl sulfur compound having a formula (IIa) or (IIb) with a halogen selected from a group of chlorine,

bromine, iodine and interhalogens, and a fluoro salt having a formula (III) to form an arylsulfur halotetrafluoride having a formula (IV).

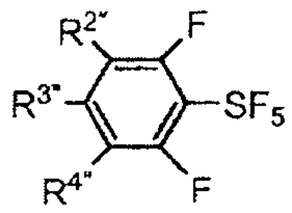
[0013] Embodiments of the present invention provide processes for producing an arylsulfur pentafluoride (formula I) by reacting an arylsulfur halotetrafluoride having a formula (IV) with a fluoride source. In some embodiments the fluoride source has a boiling point of approximately 0°C or more at 1 atm.

[0014] Finally, embodiments of the present invention provides processes for producing an arylsulfur pentafluoride (formula I) by reacting an arylsulfur halotetrafluoride having a formula (IV) with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the arylsulfur pentafluoride.

[0015] In addition, the present invention provides novel arylsulfur chlorotetrafluoride represented by formula (IV') and fluorinated arylsulfur pentafluoride represented by formula (I'):

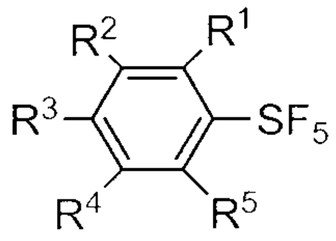


---------- (IV')



---------- (I')

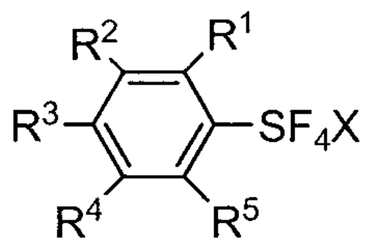
[0015a] In accordance with another aspect, there is provided a process for preparing an arylsulfur pentafluoride having a formula (I):



---------- (I)

the process comprising:

reacting an arylsulfur halotetrafluoride having a formula (IV);



(IV)

with a fluoride source, wherein the fluoride source is a solid or liquid having a boiling point of approximately 0°C or more at 1 atm, to form the arylsulfur pentafluoride;

in which: R^1, R^2, R^3, R^4, and R^5 each is independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group having 1 to 18 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a nitro group, a cyano group, a substituted or unsubstituted alkanesulfonyl group having 1 to 18 carbon atoms, a substituted or unsubstituted arenesulfonyl group having 6 to 30 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 18 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon atoms, a substituted or unsubstituted acyloxy group having from 1 to 18 carbon atoms, a substituted or unsubstituted alkanesulfonyloxy group having from 1 to 18 carbon atoms, a substituted or unsubstituted arenesulfonyloxy group having from 6 to 30 carbon atoms, a substituted or unsubstituted alkoxycarbonyl group having 2 to 18 carbon atoms, a substituted or unsubstituted aryloxycarbonyl group having 7 to 30 carbon atoms, a substituted carbamoyl group having 2 to 18 carbon atoms, a substituted amino group having 1 to 18 carbon atoms, and a SF_5 group;

and

X is a chlorine atom, a bromine atom, or an iodine atom.

[0016] These and various other features as well as advantages which characterize embodiments of the invention will be apparent from a reading of the following detailed description and a review of the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

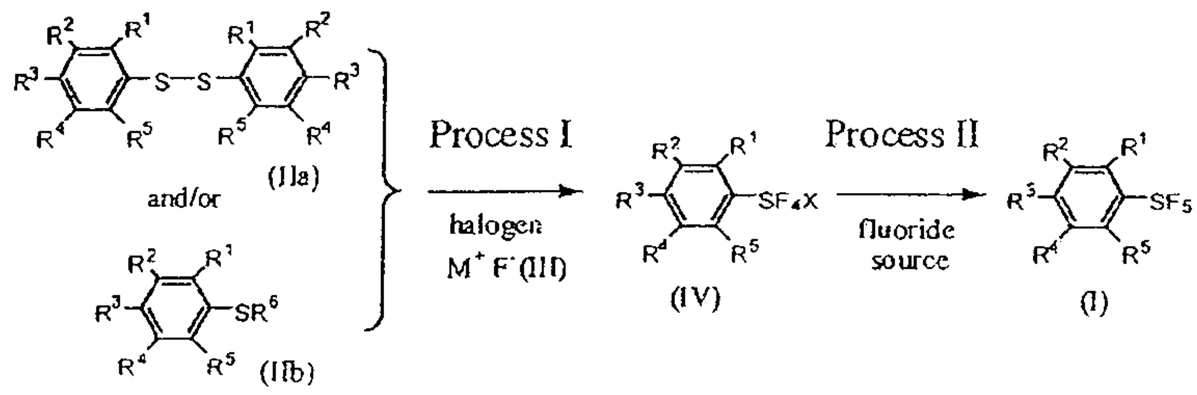
[0017] Embodiments of the present invention provide industrially useful processes for producing arylsulfur pentafluorides, as represented by formula (I). Prepared arylsulfur pentafluorides can be used, for among other things, to introduce one or more sulfur pentafluoride (SF_5) groups into various target organic compounds. Unlike previous methods in the art, the processes of the invention utilize low cost reagents to prepare moderate to excellent yields of arylsulfur pentafluoride compounds. Further, methods of the invention

provide a greater degree of overall safety in comparison to most prior art methodologies (for example the use of F_2 gas).

[0018] A distinction of the present invention is that the processes herein are accomplished at a low cost as compared to other conventional methods. For example, the reagents to perform Xe based reactions are cost prohibitive, whereas the present invention utilizes low cost materials: halogens such as Cl_2, Br_2, and I_2.

[0019] Embodiments of the invention include processes which comprise (see for example Scheme 1, Processes I and II) reacting at least one aryl sulfur compound having a formula (IIa) or a formula (IIb) with a halogen selected from the group of chlorine, bromine, iodine, and interhalogens, and a fluoro salt having a formula (III), to form an arylsulfur halotetrafluoride, represented by formula (IV). The arylsulfur halotetrafluoride is then reacted with a fluoride source to form the arylsulfur pentafluoride having a formula (I).

Scheme 1: (Processes I and II)



[0020] With regard to formulas (I), (IIa), (IIb), (III), and (IV): substituents R^1, R^2, R^3, R^4, and R^5 each is independently a hydrogen atom; a halogen atom that is a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom; a substituted or unsubstituted alkyl group having from 1 to 18 carbon atoms, preferably from 1 to 10 carbon atoms; a substituted or unsubstituted aryl group having from 6 to 30 carbon atoms, preferably from 6 to 15 carbon atoms; a nitro group; a cyano group; a substituted or unsubstituted alkanesulfonyl group having from 1 to 18 carbon atoms, preferably from 1 to 10 carbon atoms; a substituted or unsubstituted arenesulfonyl group having from 6 to 30 carbon atoms, preferably from 6 to 15 carbon atoms; a substituted or unsubstituted alkoxy group having from 1 to 18 carbon atoms, preferably from 1 to 10 carbon atoms; a substituted or unsubstituted aryloxy group having from 6 to 30 carbon atoms, preferably from 6 to 15 carbon atoms; a substituted or unsubstituted acyloxy group having from 1 to 18 carbon atom, preferably from 1 to 10 carbon atoms; a substituted or unsubstituted alkanesulfonyloxy group having from 1 to 18 carbon

atom, preferably from 1 to 10 carbon atoms; a substituted or unsubstituted arenesulfonyloxy group having from 6 to 30 carbon atoms, preferably from 6 to 15 carbon atoms; a substituted or unsubstituted alkoxycarbonyl group having 2 to 18 carbon atoms, preferably from 2 to 10 carbon atoms; a substituted or unsubstituted aryloxycarbonyl group having 7 to 30 carbon atoms, preferably from 7 to 15 carbons; a substituted carbamoyl group having 2 to 18 carbon atoms, preferably from 2 to 10 carbon atoms; a substituted amino group having 1 to 18 carbon atoms, preferably from 1 to 10 carbon atoms; and a SF_5 group; and R^6 is a hydrogen atom, a silyl group, a metal atom, an ammonium moiety, a phosphonium moiety, or a halogen atom.

[0021] With regard to M, M is a metal atom, an ammonium moiety, or a phosphonium moiety, and with regard to X, X is a chlorine atom, a bromine atom, or an iodine atom.

[0022] The term "alkyl" as used herein is linear, branched, or cyclic alkyl. The alkyl part of alkanesulfonyl, alkoxy, alkanesulfonyloxy, or alkoxycarbonyl group as used herein is also linear, branched, or cyclic alkyl part. The term "substituted alkyl" as used herein means an alkyl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0023] The term "substituted aryl" as used herein means an aryl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0024] The term "substituted alkanesulfonyl" as used herein means an alkanesulfonyl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0025] The term "substituted arenesulfonyl" as used herein means an arenesulfonyl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0026] The term "substituted alkoxy" as used herein means an alkoxy moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted aryl

group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0027] The term "substituted aryloxy" as used herein means an aryloxy moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0028] The term "substituted acyloxy" as used herein means an acyloxy moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0029] The term "substituted alkanesulfonyloxy" as used herein means an alkanesulfonyloxy moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0030] The term "substituted arenesulfonyloxy" as used herein means an arenesulfonyloxy moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0031] The term "substituted alkoxycarbonyl" as used herein means an alkoxycarbonyl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0032] The term "substituted aryloxycarbonyl" as used herein means an aryloxycarbonyl moiety having one or more substituents such as a halogen atom, a substituted or unsubstituted alkyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0033] The term "substituted carbamoyl" as used herein means a carbamoyl moiety having one or more substituents such as a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, and any other group with or without a heteroatom(s)

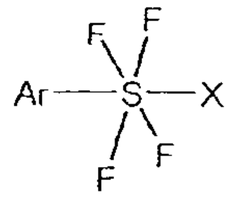
such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

[0034] The term "substituted amino" as used herein means an amino moiety having one or more substituents such as a substituted or unsubstituted acyl group, a substituted or unsubstituted alkanesulfonyl group, a substituted or unsubstituted arenesulfonyl group, and any other group with or without a heteroatom(s) such as an oxygen atom(s), a nitrogen atom(s), and/or a sulfur atom(s), which does not limit reactions of this invention.

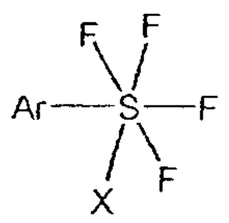
[0035] Among the substituents, R^1, R^2, R^3, R^4, and R^5, described above, a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a nitro group, a cyano group, a substituted or unsubstituted alkanesulfonyl group, a substituted or unsubstituted arenesulfonyl group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted acyloxy group, and a substituted or unsubstituted alkoxycarbonyl group are preferable, and a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, and a nitro group are more preferable from the viewpoint of availability of the starting materials.

[0036] Note that according to the nomenclature of Chemical Abstract Index Name, and in accordance with the present disclosure, for example, C_6H_5-SF_5 is named sulfur, pentafluorophenyl-; p-Cl-C_6H_4-SF_5 is named sulfur, (4-chlorophenyl)pentafluoro-; and p-CH_3-C_6H_4-SF_5 is named sulfur, pentafluoro(4-methylphenyl)-. C_6H_5-SF_4Cl is named sulfur, chlorotetrafluorophenyl-; p-CH_3-C_6H_4-SF_4Cl is named sulfur, chlorotetrafluoro(4-methylphenyl)-; and p-NO_2-C_6H_4-SF_4Cl is named sulfur, chlorotetrafluoro(4-nitrophenyl)-.

[0037] Arylsulfur halotetrafluoride compounds of formula (IV) include isomers such as trans-isomers and cis-isomers as shown below; arylsulfur halotetrafluoride is represented by $ArSF_4X$:



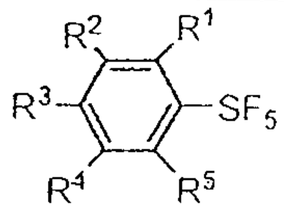
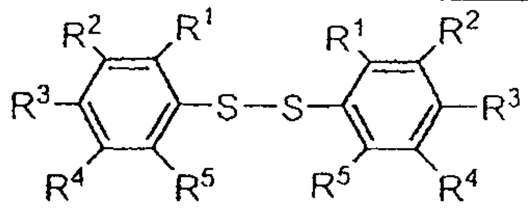
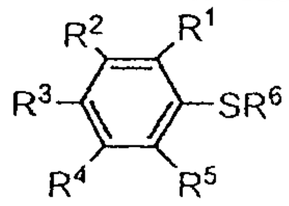
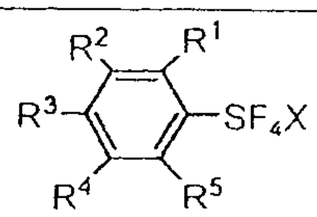
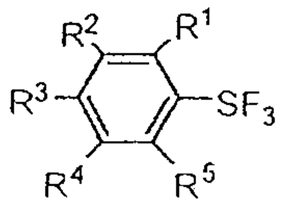
..... trans-Isomer



..... cis-Isomer

[0038] Table 1 provides structure names and formulas for reference when reviewing Schemes 1, 3~10 and Examples 1~34:

[0039] Table 1: Formulas (I~V)

Name	Structure/Formula Number
Arylsulfur pentafluoride	 ---------- (I)
Aryl sulfur compound	 ---------- (IIa)
Aryl sulfur compound	 ---------- (IIb)
Fluoro salt	M^+F^- ---------- (III)
Arylsulfur halotetrafluoride	 ---------- (IV)
Arylsulfur trifluoride	 ---------- (V)

Process I (Scheme 1)

[0040] Process I includes reacting at least one aryl sulfur compound, having a formula (IIa) or (IIb), with a halogen selected from the group of chlorine, bromine, iodine and interhalogens, and a fluoro salt (M^+F^-, formula III) to form an arylsulfur halotetrafluoride having a formula (IV).

[0041] The substituent(s), R^1, R^2, R^3, R^4, and R^5, of the products represented by the formula (IV) may be different from the substituent(s), R^1, R^2, R^3, R^4, and R^5, of the starting materials represented by the formulas (IIa) and/or (IIb). Thus, embodiments of this invention include transformation of the R^1, R^2, R^3, R^4, and R^5 to different R^1, R^2, R^3, R^4, and R^5 which may take place during the reaction of the present invention or under the reaction conditions as long as the -S-S- or -S-moiety is transformed to a $-SF_4X$ group(s).

[0042] Illustrative aryl sulfur compounds, as represented by formula (IIa), of the invention include, but are not limited to: diphenyl disulfide, each isomer of bis(fluorophenyl)

disulfide, each isomer of bis(difluorophenyl) disulfide, each isomer of bis(trifluorophenyl) disulfide, each isomer of bis(tetrafluorophenyl) disulfide, bis(pentafluorophenyl) disulfide, each isomer of bis(chlorophenyl) disulfide, each isomer of bis(dichorophenyl) disulfide, each isomer of bis(trichlorophenyl) disulfide, each isomer of bis(bromophenyl) disulfide, each isomer of bis(dibromophenyl) disulfide, each isomer of bis(iodophenyl) disulfide, each isomer of bis(chlorofluorophenyl) disulfide, each isomer of bis(bromofluorophenyl) disulfide, each isomer of bis(bromochlorophenyl) disulfide, each isomer of bis(fluoroiodophenyl) disulfide, each isomer of bis(tolyl) disulfide, each isomer of bis[(methoxymethyl)phenyl] disulfide, each isomer of bis{[(cyclohexyloxy)methyl]phenyl} disulfide, each isomer of bis[(phenylmethyl)phenyl] disulfide, each isomer of bis[(cyanomethyl)phenyl] disulfide, each isomer of bis[(nitromethyl)phenyl] disulfide, each isomer of bis{[(methanesulfonyl)methyl]phenyl} disulfide, each isomer of bis{[(benzenesulfonyl)methyl]phenyl} disulfide, each isomer of bis(ethylphenyl) disulfide, each isomer of bis[(methoxyethyl)phenyl] disulfide, each isomer of bis[(nitroethyl)phenyl] disulfide, each isomer of bis[(phenylethyl)phenyl] disulfide, each isomer of bis[chloro(methyl)phenyl] disulfide, bis[bromo(methyl)phenyl] disulfide, each isomer of bis[(trifluoromethyl)phenyl] disulfide, each isomer of bis(dimethylphenyl) disulfide, each isomer of bis[chloro(dimethyl)phenyl] disulfide, each isomer of bis[di(trifluoromethyl)phenyl] disulfide, each isomer of bis(trimethylphenyl) disulfide, each isomer of bis[chloro(trimethyl)phenyl] disulfide, each isomer of bis(tetramethylphenyl) disulfide, each isomer of bis[chloro(tetramethyl)phenyl] disulfide, bis(pentamethylphenyl) disulfide, each isomer of bis(ethylphenyl) disulfide, each isomer of bis[(2,2,2-trifluoroethyl)phenyl] disulfide, each isomer of bis[(perfluoroethyl)phenyl] disulfide, each isomer of bis(diethylphenyl) disulfide, each isomer of bis(ethylmethylphenyl) disulfide, each isomer of bis(propylphenyl) disulfide, each isomer of bis(isopropylphenyl) disulfide, each isomer of bis(butylphenyl) disulfide, each isomer of bis(sec-butylphenyl) disulfide, each isomer of bis(isobutylphenyl) disulfide, each isomer of bis(tert-butylphenyl) disulfide, each isomer of bis(cyclopropylphenyl) disulfide, each isomer of bis(cyclopentylphenyl) disulfide, each isomer of bis(cyclohexylphenyl) disulfide, each isomer of bis{[(cyclohexyl)cyclohexyl]phenyl} disulfide, each isomer of bis(biphenyl) disulfide, each isomer of bis(tolylphenyl) disulfide, each isomer of bis[(chlorophenyl)phenyl] disulfide, each isomer of bis[(bromophenyl)phenyl] disulfide, each isomer of bis[(nitrophenyl)phenyl] disulfide, each isomer of bis(terphenylyl) disulfide, each isomer of bis[(phenyl)terphenylyl] disulfide, each isomer of bis[(methanesulfonyl)phenyl] disulfide, each isomer of

bis[(trifluoromethanesulfonyl)phenyl] disulfide, each isomer of bis[(benzenesulfonyl)phenyl] disulfide, each isomer of bis[(toluenesulfonyl)phenyl] disulfide, each isomer of bis(methoxyphenyl) disulfide, each isomer of bis(ethoxyphenyl) disulfide, each isomer of bis(propoxyphenyl) disulfide, each isomer of bis(butoxyphenyl) disulfide, each isomer of bis(cyclopropylphenyl) disulfide, bis(cyclohexyloxylphenyl) disulfide, each isomer of bis[(trifluoromethoxy)phenyl] disulfide, each isomer of bis[(perfluoroethoxyl)phenyl] disulfide, each isomer of bis[(trifluoroethoxy)phenyl] disulfide, each isomer of bis[(tetrafluoroethoxy)phenyl] disulfide, each isomer of bis[(perfluoropropoxy)phenyl] disulfide, each isomer of bis(phenyloxyphenyl) disulfide, each isomer of bis(fluorophenyloxyphenyl) disulfide, each isomer of bis(chlorophenyloxyphenyl) disulfide, each isomer of bis(bromophenyloxyphenyl) disulfide, each isomer of bis(nitrophenyloxyphenyl) disulfide, each isomer of bis[(dinitrophenyloxy)phenyl] disulfide, each isomer of bis[(pentafluorophenyloxy)phenyl] disulfide, each isomer of bis(trifluoromethylphenyloxyphenyl) disulfide, each isomer of bis(cyanophenyloxyphenyl) disulfide, each isomer of bis(naphthyloxylphenyl) disulfide, each isomer of bis[(heptafluoronaphthyloxy)phenyl] disulfide, each isomer of bis[acetoxyphenyl] disulfide, each isomer of bis[(benzoyloxy)phenyl] disulfide, each isomer of bis[(methanesulfonyloxy)phenyl] disulfide, each isomer of bis[(benzenesulfonyloxy)phenyl] disulfide, each isomer of bis[(toluenesulfonyloxy)phenyl] disulfide, each isomer of bis[(methoxycarbonyl)phenyl] disulfide, each isomer of bis[(ethoxycarbonyl)phenyl] disulfide, each isomer of bis[(phenoxycarbonyl)phenyl] disulfide, each isomer of bis[(N,N-dimethylcarbamoyl)phenyl] disulfide, each isomer of bis[(N,N-diethylcarbamoyl)phenyl] disulfide, each isomer of bis[(N,N-diphenylcarbamoyl)phenyl] disulfide, each isomer of bis[(N,N-dibenzylcarbamoyl)phenyl] disulfide, each isomer of bis[(N-acetyl-N-methylamino)phenyl] disulfide, each isomer of bis[(N-acetyl-N-phenylamino)phenyl] disulfide, each isomer of bis[(N-acetyl-N-benzylamino)phenyl] disulfide, each isomer of bis[(N-benzoyl-N-methylamino)phenyl] disulfide, each isomer of bis[(N-methanesulfonyl-N-methylamino)phenyl] disulfide, each isomer of bis[(N-toluenesulfonyl-N-methylamino)phenyl] disulfide, each isomer of bis[(N-toluenesulfonyl-N-benzylamino)phenyl] disulfide, and each isomer of bis[(pentafluorosulfanyl)phenyl] disulfide. Each of the above formula (IIa) compounds is available (see for example Sigma, Acros, TCI, Lancaster, Alfa Aesar, etc.) or can be prepared in accordance with understood principles of synthetic chemistry.

[0043] Illustrative aryl sulfur compounds, as represented by formula (IIb), of the invention include, but are not limited to: benzenethiol, each isomer of fluorobenzenethiol (o-, m-, and p-fluorobenzenethiol), each isomer of chlorobenzenethiol, each isomer of bromobenzenethiol each isomer of iodobenzenethiol, each isomer of difluorobenzenethiol, each isomer of trifluorobenzenethiol, each isomer of tetrafluorobenzenethiol, pentafluorobenzenethiol, each isomer of dichlorobenzenethiol, each isomer of chlorofluorobenzenethiol, each isomer of methylbenzenethiol, each isomer of (trifluoromethyl)benzenethiol, each isomer of dimethylbenzenethiol, each isomer of bis(trifluorometyl)benzenethiol, each isomer of methyl(trifluoromethyl)benzenethiol, each isomer of trimethylbenzenethiol, each isomer of tetramethylbenzenethiol, pentamethylbenzenethiol, each isomer of ethylbenzenethiol, each isomer of (2,2,2-trifluoroethyl)benzenethiol, each isomer of (perfluoroethyl)benzenethiol, each isomer of diethylbenzenethiol, each isomer of ethylmethylbenzenethiol, each isomer of propylbenzenethiol, each isomer of isopropylbenzenethiol, each isomer of butylbenzenethiol, each isomer of sec-butylbenzenethiol, each isomer of isobutylbenzenethiol, each isomer of tert-butylbenzenethiol, each isomer of nitrobenzenethiol, each isomer of dinitrobenzenethiol, each isomer of cyanobenzenethiol, each isomer of phenylbenzenethiol, each isomer of tolylbenzenethiol, each isomer of (chlorophenyl)benzenethiol, each isomer of (bromophenyl)benzenethiol, each isomer of (nitrophenyl)benzenethiol, each isomer of (methanesulfonyl)benzenethiol, each isomer of (trifluoromethanesulfonyl)benzenethiol, each isomer of (benzenesulfonyl)benzenethiol, each isomer of (toluenesulfonyl)benzenethiol, each isomer of (methoxycarbonyl)benzenethiol, each isomer of (ethoxycarbonyl)benzenethiol, each isomer of (phenoxycarbonyl)benzenethiol, each isomer of (N,N-dimethylcarbamoyl)benzenethiol, each isomer of (N,N-diethylcarbamoyl)benzenethiol, each isomer of (N,N-dibenzylcarbamoyl)benzenethiol, each isomer of (N,N-diphenylcarbamoyl)benzenethiol, each isomer of (N-acetyl-N-methylamino)benzenethiol, each isomer of (N-acetyl-N-phenylamino)benzenethiol, each isomer of (N-acetyl-N-benzylamino)benzenethiol, each isomer of (N-benzoyl-N-methylamino)benzenethiol, each isomer of (N-methanesulfonyl-N-methylamino)benzenethiol, each isomer of (N-toluenesulfonyl-N-methylamino)benzenethiol, each isomer of (N-toluenesulfonyl-N-benzylamino)benzenethiol, and each isomer of (pentafluorosulfanyl)benzenethiol; lithium, sodium, and potassium salts of the benzenethiol compounds exemplified here; ammonium, diethylammonium, triethylammonium, trimethylammnoim, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium salts of the

benzenethiol compounds exemplified here; tetramethylphosphonium, tetraethylphosphonium, tetrapropylphosphonium, tetrabutylphosphonium, and tetraphenylphosphonium salts of the benzenethiol compounds exemplified here; and *S*-trimethylsilyl, *S*-triethylsilyl, *S*-tripropylsilyl, *S*-dimethyl-t-butylsilyl, and *S*-dimethylphenylsilyl derivative of the benzenethiol compounds exemplified here. Examples of aryl sulfur compounds of formula (IIb) where R^6 is a halogen atom are benzenesulfenyl chloride, each isomer of nitrobenzenesulfenyl chloride, each isomer of dinitrobenzenesulfenyl chloride, and other like compounds. Each of the above formula (IIb) compounds is available (see for example Sigma, Acros, TCI, Lancaster, Alfa Aesar, etc.) or can be prepared in accordance with understood principles of synthetic chemistry.

[0044] Typical halogens employable in the present invention include chlorine (Cl_2), bromine (Br_2), iodine (I_2), and interhalogens such as ClF, BrF, ClBr, ClI, Cl_3I, and BrI. Among these, chlorine (Cl_2) is preferable due to low cost.

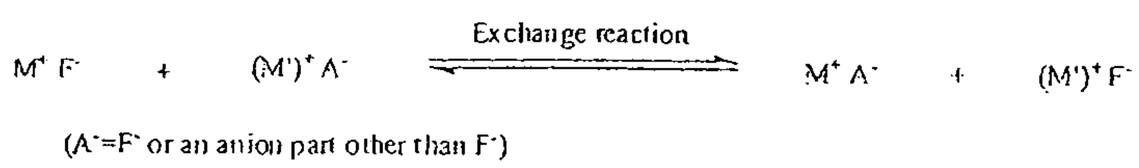
[0045] Fluoro salts, having a formula (III), are those which are easily available and are exemplified by metal fluorides, ammonium fluorides, and phosphonium fluorides. Examples of suitable metal fluorides are alkali metal fluorides such as lithium fluoride, sodium fluoride, potassium fluoride (including spray-dried potassium fluoride), rubidium fluoride, and cesium fluoride. Examples of suitable ammonium fluorides are tetramethylammonium fluoride, tetraethylammonium fluoride, tetrapropylammonium fluoride, tetrabutylammonium fluoride, benzyltrimethylammonium fluoride, benzyltriethylammonium fluoride, and so on. Examples of suitable phosphonium fluorides are tetramethylphosphonium fluoride, tetraethylphosphonium fluoride, tetrapropylphosphonium fluoride, tetrabutylphosphonium fluoride, tetraphenylphosphonium fluoride, tetratolylphosphonium fluoride, and so on. The alkali metal fluorides, such as potassium fluoride and cesium fluoride, are preferable from the viewpoint of availability and capacity to result in high yield, and potassium fluoride is most preferable from the viewpoint of cost.

[0046] As a fluoro salt (formula III), there can be used a mixture of a metal fluoride and an ammonium fluoride or a phosphonium fluoride, a mixture of an ammonium fluoride and a phosphonium fluoride, and a mixture of a metal fluoride, an ammonium fluoride, and a phosphonium fluoride.

[0047] As a fluoro salt (formula III), there can also be used a mixture of a metal fluoride and an ammonium salt having an anion part other than F^-; a mixture of a metal salt having an anion part other than F^- and an ammonium fluoride; a mixture of a metal fluoride

and a phosphonium salt having an anion part other than F^-; a mixture of a metal salt having an anion part other than F^- and a phosphonium fluoride; a mixture of an ammonium fluoride and a phosphonium salt having an anion part other than F^-; and a mixture of an ammonium salt having an anion part other than F^- and a phosphonium fluoride. Furthermore, there can be used a mixture of a metal fluoride, an ammonium fluoride, and a phosphonium salt having an anion part other than F^-; a mixture of a metal fluoride, an ammonium salt having an anion part other than F^-, and a phosphonum fluoride; a mixture of a metal salt having an anion part other than F^-, an ammonium fluoride, and a phosphonium fluoride; a mixture of a metal fluoride, an ammonium salt having an anion part other than F^-, and a phosphonium salt having an anion part other than F^-; and so on. These salts can undertake a mutual exchange reaction of the anion parts between and among these salts (for example, see Scheme 2).

Scheme 2: Mutual anion exchange reaction between salts



[0048] The combination of these salts may accelerate the reactions in Process I, because the reaction may depend on the solubility of the fluoro salts to the solvent used. As such, a high concentration of fluoride anions (F^-) will increase the available fluoride anion during the reaction. Therefore, one may choose a suitable combination of these salts in order to increase the effective concentration of F^-. The amount (used against the amount of the metal fluoride, ammonium fluorides, and/or phosphonium fluorides) of the metal, ammonium, and phosphonium salts having anion parts other than F^- can be chosen from the catalytic amounts to any amounts that do not interfere with the reactions or do not so decrease the yields of the products. The anion parts other than F^- can be chosen from any anions which do not limit the reactions or do not so decrease the yields of the products. The examples of the anion parts other than F^- are, but are not limited to, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, SO_4^-, $^-OCOCH_3$, $^-OCOCF_3$, $^-OSO_2CH_3$, $^-OSO_2CF_3$, $^-OSO_2C_4F_9$, $^-OSO_2C_6H_5$, $^-OSO_2C_6H_4CH_3$, $^-OSO_2C_6H_4Br$, and so on. Among them, the anion parts (other than F^-) which do not have an oxygen anion(s) are preferable, and Cl^-, BF_4^- and PF_6^- are more preferable because of high yield reactions. In addition, Cl^- is most preferable because of the cost.

[0049] From the viewpoint of efficiency and yields of the reactions, Process I is preferably carried out in the presence of one or more solvents. The solvent is preferably an inert, polar, aprotic solvent. The preferable solvents will not substantially react with the starting materials and reagents, the intermediates, and the final products. Suitable solvents

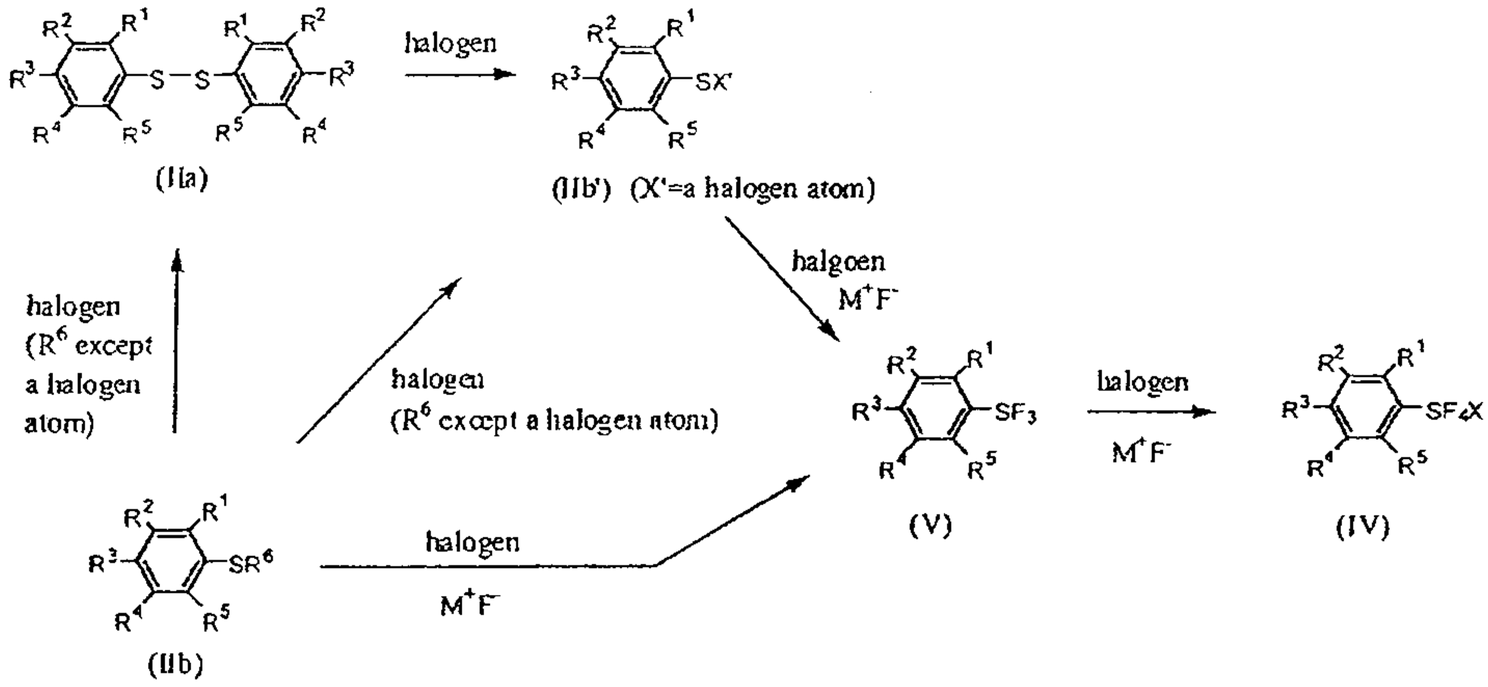
include, but are not limited to, nitriles, ethers, nitro compounds, and so on, and mixtures thereof. Illustrative nitriles are acetonitrile, propionitrile, benzonitrile, and so on. Illustrative ethers are tetrahydrofuran, diethyl ether, dipropyl ether, dibutyl ether, t-butyl methyl ether, dioxane, glyme, diglyme, triglyme, and so on. Illustrative nitro compounds are nitromethane, nitroethane, nitropropane, nitrobenzene, and so on. Acetonitrile is a preferred solvent for use in Process I from a viewpoint of providing higher yields of the products.

[0050] In order to obtain good yields of product in Process I, the reaction temperature can be selected in the range of about -60°C ~ +70°C. More preferably, the reaction temperature can be selected in the range of about -40°C ~ +50°C. Furthermore preferably, the reaction temperature can be selected in the range of about -20°C ~ +40°C.

[0051] Reaction conditions of Process I are optimized to obtain economically good yields of product. In one illustrative embodiment, from about 5 mol to about 20 mol of halogen are combined with about 1 mol of aryl sulfur compound (formula IIa) to obtain a good yield of arylsulfur halotetrafluorides (formula IV). In another embodiment, from about 3 to about 12 mol of halogen are combined with 1 mol of aryl sulfur compound of formula IIb (R^6=a hydrogen atom, a silyl group, a metal atom, an ammonium moiety, or a phosphonium moiety) to obtain good yields of arylsulfur halotetrafluorides (formula IV). From about 2 to about 8 mol of halogen are combined with 1 mol of aryl sulfur compound of formula IIb (R^6=a halogen atom) to obtain good yields of arylsulfur halotetrafluorides (formula IV). The amount of a fluoro salt (formula III) used in embodiments of Process I can be in the range of from about 8 to about 24 mol against 1 mol of aryl sulfur compound of formula (IIa) to obtain economically good yields of product. The amount of a fluoro salt (formula III) used in embodiments of Process I can be in the range of from about 4 to about 12 mol against 1 mol of aryl sulfur compound of formula (IIb) to obtain economically good yields of product.

[0052] Note that the reaction time for Process I varies dependent upon reaction temperature, and the types and amounts of substrates, reagents, and solvents. As such, reaction time is generally determined as the amount of time required to complete a particular reaction, but can be from about 0.5 h to several days, preferably, within a few days.

[0053] **Scheme 3: Reaction mechanism for Process I**



[0054] A more complete reaction mechanism of Process I is shown in Scheme 3 above. Aryl sulfur compound of formula (IIa) reacts with halogen to form arylsulfur halide (IIb'=IIb when R^6=a halogen atom), which then reacts with halogen and fluoro salt (M^+F^-) to form arylsulfur trifluoride (formula V). The arylsulfur trifluoride further reacts with halogen and fluoro salt to give the arylsulfur halotetrafluoride (formula (IV)). As such, the compounds as represented by formula (V) act as intermediates in the formation of compounds of formula (IV). The compounds as represented by formula (IIb') also act as intermediates. The starting aryl sulfur compound of formula (IIb when R^6=a halogen atom) reacts with halogen and fluoro salt to form the arylsulfur trifluoride. Aryl sulfur compounds as represented by formula (IIb when R^6=a hydrogen atom, a metal atom, an ammonium moiety, or a phosphonium moiety) react with halogen to form aryl sulfur compounds as represented by formula (IIa) or formula (IIb'), which then reacts with halogen and fluoro salt to give the arylsulfur trifluoride (formula V). As such, the compounds as represented by formula (IIa) or (IIb') act as intermediates in the formation of compounds of formula (IV) from aryl sulfur compounds of formula (IIb, R^6 except for a halogen atom). The reaction mechanism for the production of arylsulfur halotetrafluoride (formula IV) via arylsulfur trifluoride (formula V) was confirmed by ^{19}F NMR of an intermediate reaction mixture. In addition, the arylsulfur trifluoride can be converted to the arylsulfur halotetrafluoride (formula IV) under the similar reaction conditions as demonstrated by at least Example 14.

Process II (Scheme 1)

[0055] Embodiments of the invention include Process II: a reaction of arylsulfur halotetrafluoride, obtained by the process I, with a fluoride source, as shown in Scheme 1.

[0056] The substituent(s), R^1, R^2, R^3, R^4, and R^5, of the products represented by the formula (I) may be different from the substituent(s), R^1, R^2, R^3, R^4, and R^5, of the materials represented by the formula (IV). Thus, embodiments of this invention include transformation of the R^1, R^2, R^3, R^4, and R^5 to different R^1, R^2, R^3, R^4, and R^5 which may take place during the reaction of the present invention or under the reaction conditions as long as the $-SF_4X$ is transformed to a $-SF_5$ group.

[0057] Fluoride sources employable in Process II are anhydrous compounds that display fluoride activity to the arylsulfur halotetrafluoride (formula IV). The fluoride sources can be selected from fluorides of typical elements in the Periodic Table, fluorides of transition elements in the Periodic Table, and mixture or compounds between or among these fluorides of typical elements and/or transition elements. The fluoride source may be a mixture, salt, or complex with an organic molecule(s) that does(do) not limit the reactions of this invention. The fluoride sources also include mixtures or compounds of fluoride sources with fluoride source-activating compounds such as $SbCl_5$, $AlCl_3$, PCl_5, BCl_3, and so on. Process II can be carried out using one or more fluoride sources.

[0058] Suitable examples of fluorides of the typical elements include fluorides of Element 1 in the Periodic Table such as hydrogen fluoride (HF) and alkali metal fluorides, LiF, NaF, KF, RbF, and CsF; fluorides of Element 2 (alkaline earth metal fluorides) such as BeF_2, MgF_2, MgFCl, CaF_2, SrF_2, BaF_2 and so on; fluorides of Element 13 such as BF_3, BF_2Cl, $BFCl_2$, AlF_3, AlF_2Cl, $AlFCl_2$, GaF_3, InF_3, and so on; fluorides of Element 14 such as SiF_4, SiF_3Cl, SiF_2Cl_2, $SiFCl_3$, GeF_4, GeF_2Cl_2, SnF_4, PbF_2, PbF_4, and so on; fluorides of Element 15 such as PF_5, AsF_5, SbF_3, SbF_5, SbF_4Cl, SbF_3Cl_2, SbF_2Cl_3, $SbFCl_4$, BiF_5, and so on; fluorides of Element 16 such as OF_2, SeF_4, SeF_6, TeF_4, TeF_6, and so on; fluorides of Element 17 such as F_2, ClF, ClF_3, BrF, BrF_3, IF_6, and so on.

[0059] Suitable examples of fluorides of the transition elements (transition meal fluorides) include fluorides of Element 3 in the Periodic Table such as ScF_3, YF_3, LaF_3, and so on; fluorides of Element 4 such as TiF_4, ZrF_3, ZrF_4, HfF_4, and so on; fluorides of Element 5 such as VF_3, VF_5, NbF_5, TaF_5, and so on; fluorides of Element 6 such as CrF_3, MoF_6, WF_6, and so on; fluorides of Element 7 such as MnF_2, MnF_3, ReF_6, and so on; fluorides of Element 8 such as FeF_3, RuF_3, RuF_4, OsF_4, OsF_5, OsF_6, and so on; fluorides of Element 9 such as CoF_2, CoF_3, RhF_3, IrF_6, and so on; fluorides of Element 10 such as NiF_2, PdF_2, PtF_2, PtF_4,

PtF_6, and so on; fluorides of Element 11 such as CuF_2,CuFCl, AgF, AgF_2, and so on; fluorides of Element 12 such as ZnF_2, ZnFCl, CdF_2, HgF_2, and so on.

[0060] Suitable examples of mixture or compounds between or among the fluorides of typical elements and/or transition elements include, but are not limited to, HBF_4 [a compound of hydrogen fluoride (HF) and BF_3], HPF_6, $HAsF_6$, $HSbF_6$, LiF/HF [a mixture or salt of lithium fluoride(LiF) and hydrogen fluoride(HF)], NaF/HF, KF/HF, CsF/HF, $(CH_3)_4NF/HF$, $(C_2H_5)_4NF/HF$, $(C_4H_9)_4NF/HF$, ZnF_2/HF, CuF_2/HF, SbF_5/SbF_3, $SbF_5/SbF_3/HF$, ZnF_2/SbF_5, $ZnF_2/SbF_5/HF$, KF/SbF_5, $KF/SbF_5/HF$, and so on.

[0061] Suitable examples of mixtures, salts, or complexes of the fluorides with organic molecules include, but are not limited to, BF_3 diethyl etherate [$BF_3 \cdot O(C_2H_5)_2$], BF_3 dimethyl etherate, BF_3 dibutyl etherate, BF_3 tetrahydrofuran complex, BF_3 acetonitrile complex ($BF_3 \cdot NCCH_3$), HBF_4 diethyl etherate, HF/pyridine (a mixture of hydrogen fluoride and pyridine), HF/methylpyridine, HF/dimethylpyridine, HF/trimethylpyridine, HF/trimethylamine, HF/triethylamine, HF/dimethyl ether, HF/diethyl ether, and so on. As HF/pyridine, a mixture of about 70wt% hydrogen fluoride and about 30wt% pyridine is preferable because of availability.

[0062] Among these examples of fluoride sources mentioned above, transition metal fluorides, fluorides of the Elements 13~15, hydrogen fluoride, and mixtures or compounds thereof, and mixtures, salts, or complexes of these fluorides with organic molecules are preferable.

[0063] Among the transition metal fluorides, the fluorides of Elements 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) are exemplified preferably. ZnF_2 and CuF_2 are furthermore preferable from the viewpoint of practical operation, yields, and cost. Among the fluorides of the Elements 13~15, BF_3, AlF_3, AlF_2Cl, SbF_3, SbF_5, SbF_4Cl, and SbF_3Cl_2 are preferably exemplified. Fluorides of Elements 13~15 can be used preferably for the preparation of polyfluorinated arylsulfur pentafluorides. Among the organic molecules usable for the mixtures, salts, or complexes with the fluorides, pyridine, ethers such as dimethyl ether, diethyl ether, dipropyl ether, and diisopropyl ether, alkylamines such as trimethylamine and triethylamine, and nitriles such as acetonitrile and propionitrile are preferable. Among these, pyridine, diethyl ether, triethylamine, and acetonitrile are more preferable because of availability and cost.

[0064] In some cases, since the reaction of an arylsulfur halotetrafluoride and a fluoride source can be slowed down by flowing an inactive gas such as nitrogen (see

Examples 18 and 19), it is not preferable that the vapor on the reaction mixture and/or the gas which may be generated from the reaction mixture be removed, for example by flowing an inactive gas on or through the reaction mixture or other methods. This was an unexpected finding discovered by the inventor, as one would not expect removal of the reaction vapor to slow the reaction. Therefore, there is a case that it is preferable that the reaction be carried out in a closed or sealed reactor, by maintaining the reactor at a constant pressure, or by equipping the reactor with a balloon filled with an inactive gas such as nitrogen, or in any other like manner. In this manner, embodiments of the invention facilitate the presence of the reaction vapor.

[0065] Process II can be carried out with or without a solvent. However, in many cases, unlike most organic reactions, the present invention typically does not require a solvent. This presents an added advantage to performing embodiments of the invention (due to lower cost, no solvent separating requirements, etc). In some cases, the use of solvent is preferable for mild and efficient reactions. Where a solvent is utilized, alkanes, halocarbons, ethers, nitriles, nitro compounds can be used. Example alkanes include normal, branched, cyclic isomers of pentane, hexane, heptane, octane, nonane, decane, dodecan, undecane, and other like compounds. Illustrative halocarbons include dichloromethane, chloroform, carbon tetrachloride, dichloroethane, trichloroethane, terachloroethane, trichlorotrifluoroethane, chlorobenzene, dichlorobenzene, trichlorobenzene, hexafluorobenzene, benzotrifluoride, bis(trifluoromethyl)benzene, perfluorohexane, perfluorocyclohexane, perfluoroheptane, perfluorooctane, perfluorononane, perfluorodecane, perfluorodecalin, and other like compounds. Illustrative ethers include diethyl ether, dipropyl ether, di(isopropyl) ether, dibutyl ether, t-butyl methyl ether, dioxane, glyme (1,2-dimethoxyethane), diglyme, triglyme, and other like compounds. Illustrative nitriles include acetonitrile, propionitrile, benzonitrile, and other like compounds. Illustrative nitro compounds include nitromethane, nitroethane, nitrobenzene, and other like compounds. Where the fluoride source used for the reaction is liquid, it can be used as both a reactant and a solvent. A typical example of this is hydrogen fluoride and a mixture of hydrogen fluoride and pyridine. Hydrogen fluoride and a mixture of hydrogen fluoride and pyridine may be usable as a solvent.

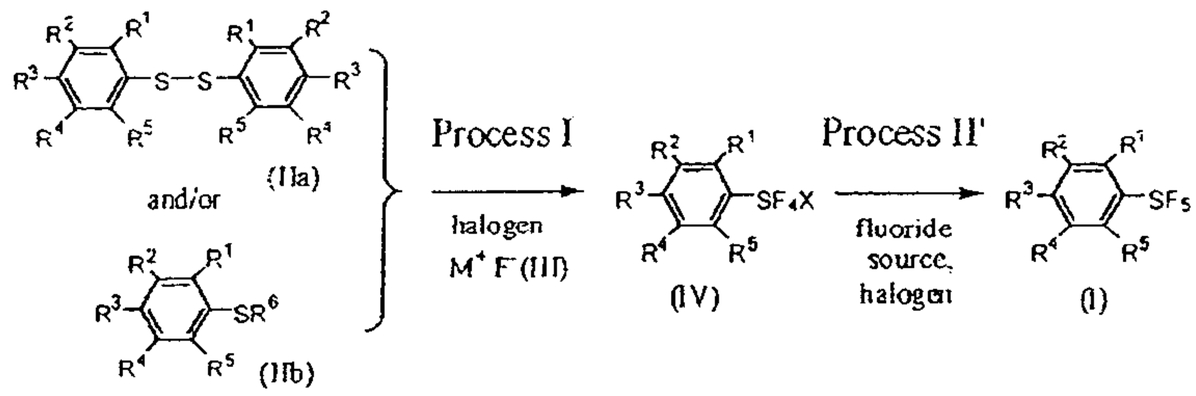
[0066] In order to optimize yield with regard to Process II, the reaction temperature is selected in the range of from about -100°C to about +250°C. More typically, the reaction temperature is selected in the range of from about -80°C to about +230°C. Most typically, the reaction temperature is selected in the range of from about -60°C to about +200°C.

[0067] In order to obtain economically good yields of the products, the amount of a fluoride source which provides n number of reactive fluoride (employable for the reaction) per molecule can be selected in the range of from about 1/n to about 20/n mol against 1 mol of arylsulfur halotetrafluoride (see formula IV). More typically, the amount can be selected in the range of from about 1/n to about 10/n mol from the viewpoint of yield and cost, as less amounts of a fluoride source decrease the yield(s) and additional amounts of a fluoride source do not significantly improve the yield(s).

[0068] As described in Process I, the reaction time of Process II also varies dependent on reaction temperature, the substrates, reagents, solvents, and their amounts used. Therefore, one can modify reaction conditions to determine the amount of time necessary for completing the reaction of Process II, but can be from about 0.1 h to several days, preferably, within a few days.

[0069] Embodiments of the invention include processes which comprise (see for example Scheme 4, Processes I and II') reacting at least one aryl sulfur compound having a formula (IIa) or a formula (IIb) with a halogen selected from the group of chlorine, bromine, iodine, and interhalogens, and a fluoro salt having a formula (III), to form an arylsulfur halotetrafluoride, represented by formula (IV). The arylsulfur halotetrafluoride is then reacted with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the arylsulfur pentafluoride as represented by a formula (I).

Scheme 4 (Processes I and II')



[0070] Process I is as described above.

[0071] Process II' is the same as Process II above except for the following modifications: The reaction of an arylsulfur halotetrafluoride and a fluoride source can be accelerated by a halogen selected from the group of chlorine, bromine, iodine, and interhalogens (see Examples 15~17).

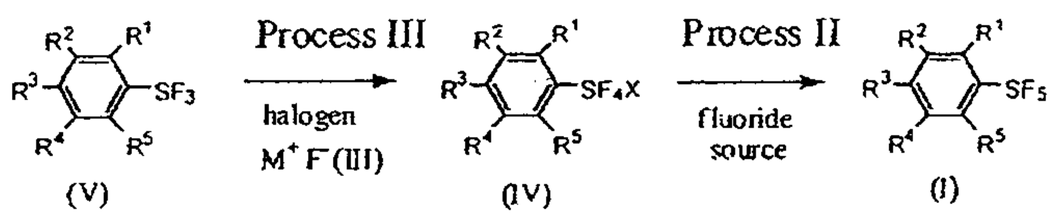
[0072] The substituent(s), R^1, R^2, R^3, R^4, and R^5, of the products represented by the formula (I) may be different from the substituent(s), R^1, R^2, R^3, R^4, and R^5, of the materials represented by the formula (IV). Thus, embodiments of this invention include transformation of the R^1, R^2, R^3, R^4, and R^5 to different R^1, R^2, R^3, R^4, and R^5 which may take place during the reaction of the present invention or under the reaction conditions as long as the $-SF_4X$ is transformed to a $-SF_5$ group.

[0073] The acceleration of the reactions by the presence of a halogen in some cases was an unexpected and surprising finding as discovered by the inventor. While not wanting to be tied to a particular mechanism, it is believed that the halogen activates a fluoride source and/or prevents disproportionation of an arylsulfur halotetrafluoride (formula IV) which may occur during this reaction. Therefore, other fluoride source-activating and/or disproportionation-preventing compounds are within the scope of the invention. The reaction in the presence of the halogen may be carried out by methods such as by adding a halogen to the reaction mixture, dissolving a halogen in the reaction mixture, flowing a halogen gas or vapor into the reaction mixture or the reactor, or others like means. Among the halogens, chlorine (Cl_2) is preferable because of cost.

[0074] The amount of halogen is from a catalytic amount to an amount in large excess. From the viewpoint of cost, a catalytic amount to 5 mol of the halogen, can be preferably selected against 1 mol of arylsulfur halotetrafluoride (formula IV).

[0075] Embodiments of the present invention include a process (Process III) which comprises reacting an arylsulfur trifluoride having a formula (V) with a halogen (chlorine, bromine, iodine, or interhalogens) and a fluoro salt having a formula (III) to form an arylsulfur halotetrafluoride having a formula (IV) and (Process II) reacting the obtained arylsulfur halotetrafluoride with a fluoride source to form the arylsulfur pentafluoride having a formula (I). Scheme 5 showing Processes III and II are shown as follows:

Scheme 5 (Processes III and II)



[0076] With regard to formulas (I), (III), (IV), and (V), R^1, R^2, R^3, R^4, R^5, R^6, M and X have the same meaning as defined above.

Process III (Scheme 5)

[0077] Embodiments of the present invention provide processes for producing arylsulfur pentafluorides (formula I) by reacting an arylsulfur trifluoride having a formula (V) with a halogen selected from the group of chlorine, bromine, iodine, and interhalogens and a fluoro salt (formula III) to form an arylsulfur halotetrafluoride having a formula (IV).

[0078] The substituent(s), R^1, R^2, R^3, R^4, and R^5, of the products represented by the formula (IV) may be different from the substituent(s), R^1, R^2, R^3, R^4, and R^5, of the starting materials represented by the formula (V). Thus, embodiments of this invention include transformation of the R^1, R^2, R^3, R^4, and R^5 to different R^1, R^2, R^3, R^4, and R^5 which may take place during the reaction of the present invention or under the reaction conditions as long as the $-SF_3$ is transformed to a $-SF_4X$.

[0079] Illustrative arylsulfur trifluorides, as represented by formula (V), of the invention can be prepared as described in the literature [see J. Am. Chem. Soc., Vol. 84 (1962), pp. 3064-3072, and Synthetic Communications Vol. 33 (2003), pp.2505-2509] and are exemplified, but are not limited, by phenylsulfur trifluoride, each isomer of fluorophenylsulfur trifluoride, each isomer of difluorophenylsulfur trifluoride, each isomer of trifluorophenylsulfur trifluoride, each isomer of tetrafluorophenylsulfur trifluoride, pentafluorophenylsulfur trifluoride, each isomer of chlorophenylsulfur trifluoride, each isomer of bromophenylsulfur trifluoride, each isomer of chlorofluorophenylsulfur trifluoride, each isomer of bromofluorophenylsulfur trifluoride, each isomer of tolylsulfur trifluoride, each isomer of chloro(methyl)phenylsulfur trifluoride, each isomer of dimethylphenylsulfur trifluoride, each isomer of chloro(dimethyl)phenylsulfur trifluoride, each isomer of trimethylphenylsulfur trifluoride, each isomer of ethylphenylsulfur trifluoride, each isomer of propylphenylsulfur trifluoride, each isomer of butylphenylsulfur trifluoride, each isomer of nitrophenylsulfur trifluoride, each isomer of dinitrophenylsulfur trifluoride, and so on.

[0080] As mentioned in the reaction mechanism for the Process I, arylsulfur trifluorides (formula V) can be the intermediates in the Process I.

[0081] A halogen employable in the present invention for Process III is the same as for Process I described above except for the amount used for the reaction.

[0082] Fluoro salts having a formula (III) for Process III are the same as for Process I described above except for the amount used in the reaction.

[0083] It is preferable that the reaction of Process III be carried out using a solvent. Examples of suitable solvents are the same as for Process I described above.

[0084] In order to economically get good yields of the products, the reaction temperature for Process III can be selected in the range of -60°C ~ +70°C. More preferably, the temperature can be selected in the range of -40°C ~ +50°C. Furthermore preferably, the temperature can be selected in the range of -20°C ~ +40°C.

[0085] In order to get good economic yields of product, the amount of a halogen used can be preferably selected in the range of from about 1 to about 5 mol, more preferably from about 1 to about 3 mol, against 1 mol of arylsulfur trifluoride (V).

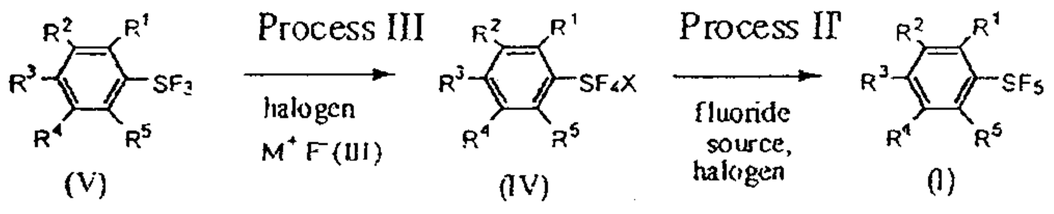
[0086] In order to get good economic yield of the products, the amount of fluoro salt (III) used can be preferably selected in the range of about 1 to about 5 mol against 1 mol of arylsulfur trifluoride (V).

[0087] The reaction time for Process III is dependent on reaction temperature, the substrates, reagents, solvents, and their amounts used. Therefore, one can choose the time necessary for completing each reaction based on modification of the above parameters, but can be from about 0.5 h to several days, preferably, within a few days.

[0088] Process II is as described above.

[0089] Embodiments of the present invention include a process (Process III) which comprises reacting an arylsulfur trifluoride having a formula (V) with a halogen (chlorine, bromine, iodine, or interhalogens) and a fluoro salt having a formula (III) to form an arylsulfur halotetrafluoride having a formula (IV) and (Process II') reacting the obtained arylsulfur halotetrafluoride with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the arylsulfur pentafluoride having a formula (I). Scheme 6 showing Processes III and II' are shown as follows:

Scheme 6 (Processes III and II')



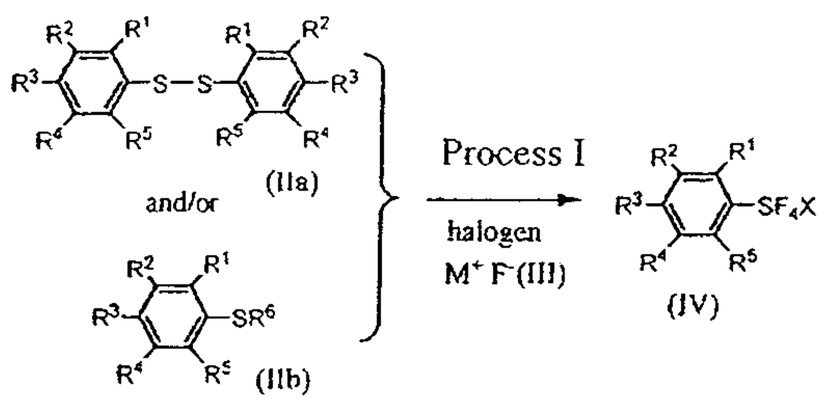
[0090] With regard to formulas (I), (III), (IV), and (V), R^1, R^2, R^3, R^4, R^5, R^6, M and X have the same meaning as defined above.

[0091] Processes III and II' are as described above.

[0092] Furthermore, the present invention includes a process (Scheme 7, Process I) for preparing an arylsulfur halotetrafluoride having a formula (IV), which comprises reacting

at least one aryl sulfur compound having a formula (IIa) or a formula (IIb) with a halogen selected from the group of chlorine, bromine, iodine, and interhalogens and a fluoro salt having a formula (III) to form the arylsulfur halotetrafluoride.

Scheme 7 (Process I)

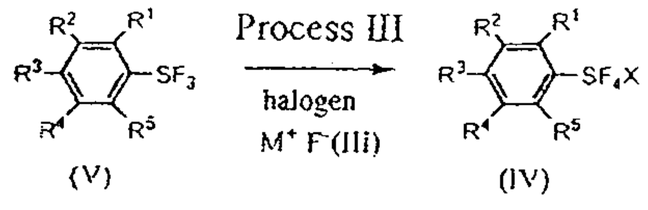


[0093] In the formulas (IIa), (IIb), (III), and (IV), R^1, R^2, R^3, R^4, R^5, R^6, M and X represent the same meaning as defined above.

[0094] Process I is described above.

[0095] Furthermore, the present invention includes a process (Scheme 8, Process III) for preparing an arylsulfur halotetrafluoride having a formula (IV), which comprises reacting an arylsulfur trifluoride having a formula (V) with a halogen selected from the group of chlorine, bromine, iodine, and interhalogens and a fluoro salt having a formula (III) to form the arylsulfur halotetrafluoride.

Scheme 8 (Process III)

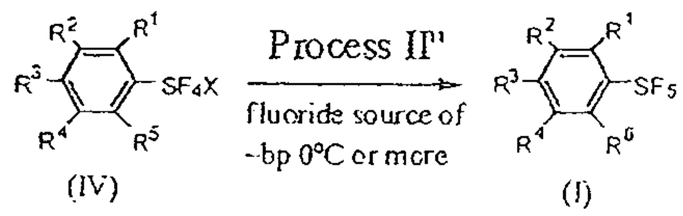


[0096] In the formulas (III), (IV), and (V), R^1, R^2, R^3, R^4, R^5, M and X represent the same meaning as defined above.

[0097] Process III is as described above.

[0098] Furthermore, the present invention includes a process (Scheme 9, Process II'') for preparing an arylsulfur pentafluoride having a formula (I), which comprises reacting an arylsulfur halotetrafluoride having a formula (IV) with a fluoride source whose boiling point is approximately 0°C or more to form the arylsulfur pentafluoride.

Scheme 9 (Process II'')



(IV) (I)

[0099] In the formulas (I) and (IV), R^1, R^2, R^3, R^4, R^5, and X represent the same meaning as defined above.

Process II'' (Scheme 9)

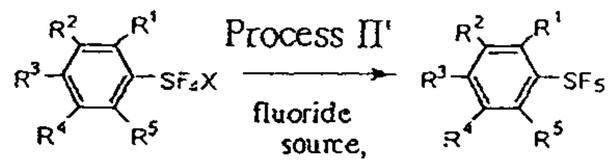
[00100] Process II'' is a reaction of arylsulfur halotetrafluoride having a formula (IV) with a fluoride source whose boiling point is approximately 0°C or more at 1 atm, as shown in Scheme 9.

[00101] The substituent(s), R^1, R^2, R^3, R^4, and R^5, of the products represented by the formula (I) may be different from the substituents, R^1, R^2, R^3, R^4, and R^5, of the starting materials represented by the formula (IV). Thus, embodiments of this invention include transformation of the R^1, R^2, R^3, R^4, and R^5 to different R^1, R^2, R^3, R^4, and R^5 which may take place during the reaction of the present invention or under the reaction conditions as long as the $-SF_4X$ is transformed to a $-SF_5$ group.

[00102] Process II'' is the same as Process II described above, and, the fluoride sources employable in Process II'' are the same as the fluoride sources previously discussed with reference to Process II, with exception that Process II'' fluoride sources have boiling points equal to or above 0°C at 1 atm.

[00103] Furthermore, the present invention includes a process (Scheme 10, Process II') for preparing an arylsulfur pentafluoride having a formula (I), which comprises reacting an arylsulfur halotetrafluoride having a formula (IV) with a fluoride source in the presence of a halogen selected from the group of chlorine, bromine, iodine, and interhalogens to form the aryl sulfurpentafluoride.

Scheme 10 (Process II')



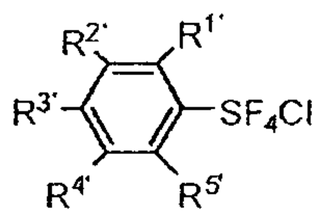
(IV) (I)

[00104] For formulas (I) and (IV), R^1, R^2, R^3, R^4, R^5, and X represent the same meaning as defined above.

[00105] Process II' is as described above.

[00106] According to the present invention, the arylsulfur pentafluorides having the formula (I) can be easily and cost-effectively produced from easily available starting materials.

[00107] The present invention provides novel arylsulfur chlorotetrafluorides represented by formula (IV') as useful intermediates;

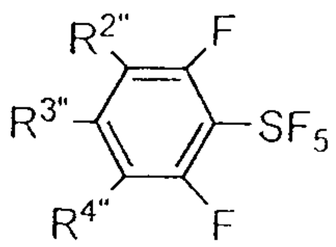


(IV')

wherein $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, and $R^{5'}$ each is independently a hydrogen atom, a halogen atom, a linear or branched alkyl group having one to four carbon atoms, or a nitro group; and where, when $R^{3'}$ is a hydrogen atom, a methyl group, or a nitro group, at least one of $R^{1'}$, $R^{2'}$, $R^{4'}$, and $R^{5'}$ is a halogen atom, a linear or branched alkyl group having one to four carbon atoms, or a nitro group. The halogen atom here is a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom.

Among these, each isomer of tert-butylphenylsulfur chlorotetrafluoride, each isomer of fluorophenylsulfur chlorotetrafluoride, each isomer of chlorophenylsulfur chlorotetrafluoride, each isomer of bromophenylsulfur chlorotetrafluoride, each isomer of difluorophenylsulfur chlorotetrafluoride, each isomer of trifluorophenylsulfur chlorotetrafluoride, and 2,3,4,5,6-pentafluorophenylsulfur chlorotetrafluoride are preferable, and 4-tert-butylphenylsulfur chlorotetrafluoride, 4-fluorophenylsulfur chlorotetrafluoride, 2-fluorophenylsulfur chlorotetrafluoride, 4-chlorophenylsulfur chlorotetrafluoride, 4-bromophenylsulfur chlorotetrafluoride, 3-bromophenylsulfur chlorotetrafluoride, 2,6-difluorophenylsulfur chlorotetrafluoride, 2,4,6-trifluorophenylsulfur chlorotetrafluoride, and 2,3,4,5,6-pentafluorophenylsulfur chlorotetrafluoride are more preferable.

The present invention also provides novel and useful fluorinated arylsulfur pentafluorides represented by formula (I');



(I')

wherein at least one of $R^{2"}$, $R^{3"}$, and $R^{4"}$ are a halogen atom and the remainders are a hydrogen atom. The halogen atom here is a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom.

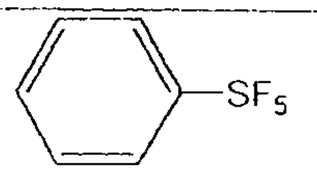
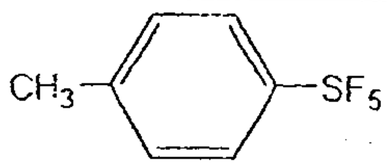
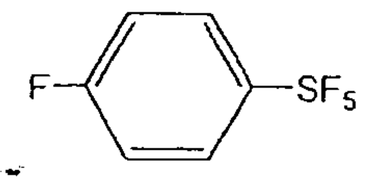
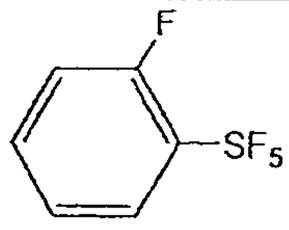
Among these, 2,3,4,5,6-pentafluorophenylsulfur pentafluoride, 2,4,6-trifluorophenylsulfur pentafluoride, 3-chloro-2,4,6-trifluorophenylsulfur pentafluoride, and 3-chloro-2,6-difluorophenylsulfur pentafluoride are preferable.

[00108] The following examples will illustrate the present invention in more detail, but it should be understood that the present invention is not deemed to be limited thereto.

EXAMPLES

[00109] The following examples are provided for illustrative purposes only and are not intended to limit the scope of the invention. Table 2 provides structure names and formulas for reference when reviewing the following examples:

Table 2: Arylsulfur Halotetrafluorides (Formulas Ia,b,d-n and IVa-j,l,n):

Formula Number	Name	Structure
Ia	Phenylsulfur pentafluoride	
Ib	p-Methylphenylsulfur pentafluoride	
Id	p-Fluorophenylsulfur pentafluoride	
Ie	o-Fluorophenylsulfur pentafluoride	

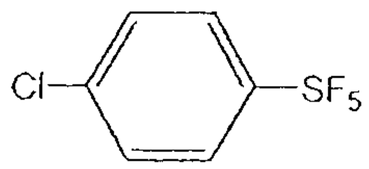
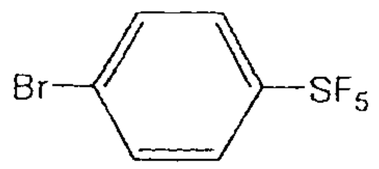
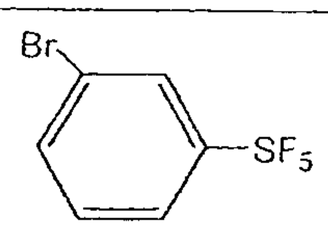
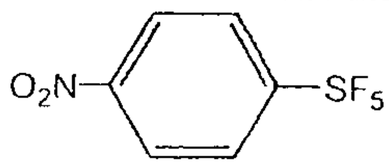
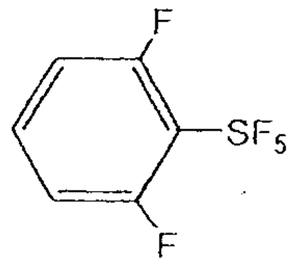
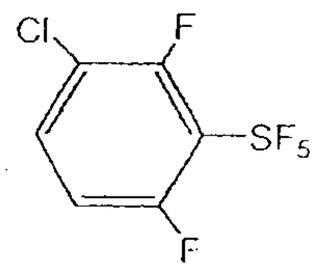
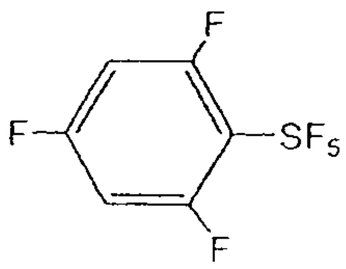
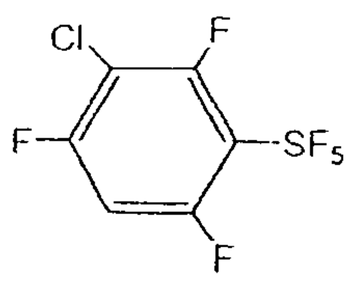
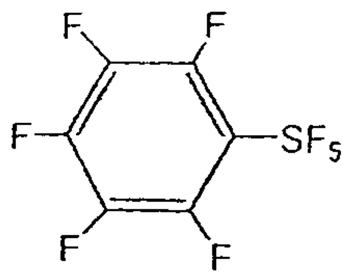
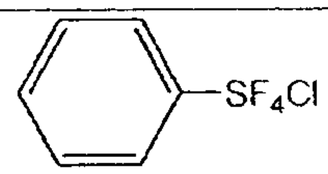
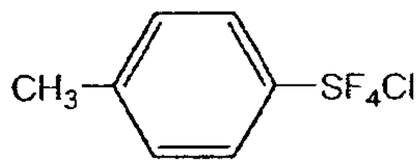
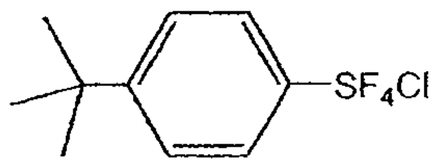
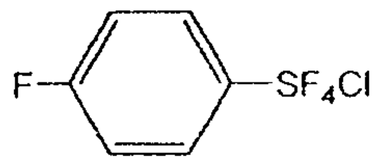
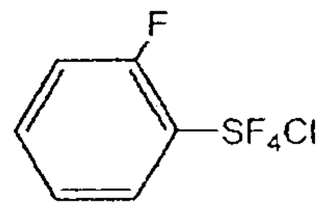
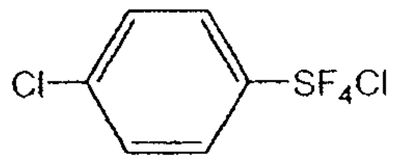
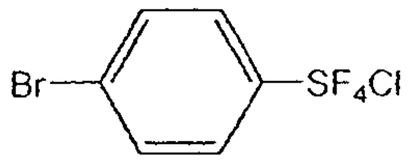
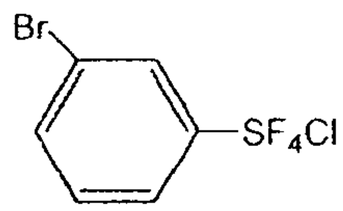
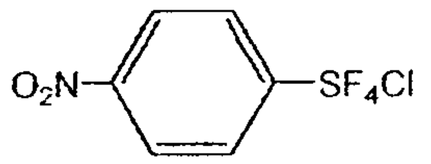
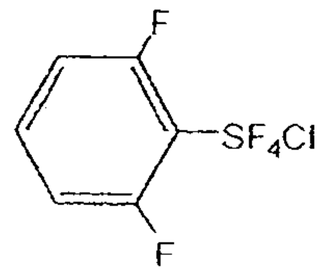
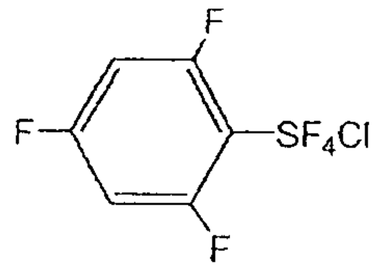
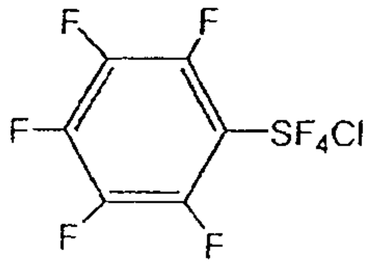
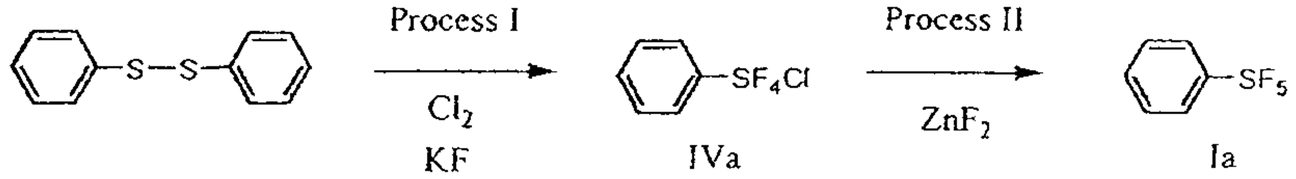
If	p-Chlorophenylsulfur pentafluoride	
Ig	p-Bromophenylsulfur pentafluoride	
Ih	m-Bromophenylsulfur pentafluoride	
Ii	p-Nitrophenylsulfur pentafluoride	
Ij	2,6-Difluorophenylsulfur pentafluoride	
Ik	3-Chloro-2,6-difluorophenylsulfur pentafluoride	
Il	2,4,6-Trifluorophenylsulfur pentafluoride	
Im	3-Chloro-2,4,6-trifluorophenylsulfur pentafluoride	
In	2,3,4,5,6-Pentafluorophenylsulfur pentafluoride	

Table 2 (continued)

Formula Number	Name	Structure
IVa	Phenylsulfur chlorotetrafluoride	
IVb	p-Methylphenylsulfur chlorotetrafluoride	
IVc	p-(tert-Butyl)phenylsulfur chlorotetrafluoride	
IVd	p-Fluorophenylsulfur chlorotetrafluoride	
IVe	o-Fluorophenylsulfur chlorotetrafluoride	
IVf	p-Chlorophenylsulfur chlorotetrafluoride	
IVg	p-Bromophenylsulfur chlorotetrafluoride	
IVh	m-Bromophenylsulfur chlorotetrafluoride	
IVi	p-Nitrophenylsulfur chlorotetrafluoride	

IVj	2,6-Difluorophenylsulfur chlorotetrafluoride	
IVl	2,4,6-Trifluorophenylsulfur chlorotetrafluoride	
IVn	2,3,4,5,6-Pentafluorophenylsulfur chlorotetrafluoride	

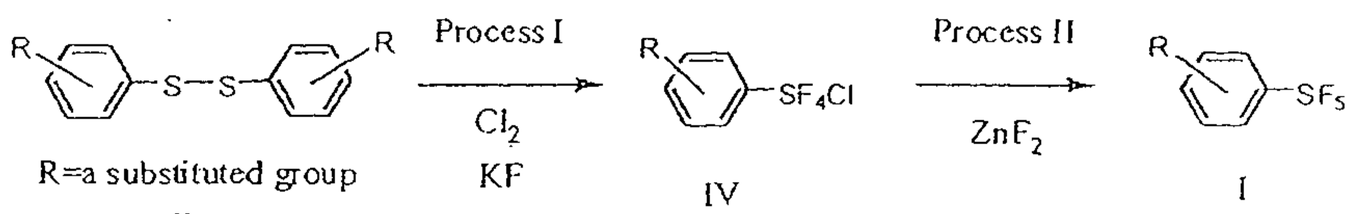
Example 1. Synthesis of phenylsulfur pentafluoride from diphenyl disulfide



[00110] (Process I) A 500 mL round bottom glassware flask was charged with diphenyl disulfide (33.0 g, 0.15 mol), dry KF (140 g, 2.4 mol) and 300 mL of dry CH_3CN. The stirred reaction mixture was cooled on an ice/water bath under a flow of N_2 (18 mL/min). After N_2 was stopped, chlorine (Cl_2) was bubbled into a reaction mixture at the rate of about 70 mL/min. The Cl_2 bubbling took about 6.5 h. The total amount of Cl_2 used was about 1.2 mol. After Cl_2 was stopped, the reaction mixture was stirred for additional 3 h. N_2 was then bubbled through for 2 hours to remove an excess of Cl_2. The reaction mixture was then filtered with 100 mL of dry hexanes in air. About 1 g of dry KF was added to the filtrate. The KF restrains possible decomposition of the product. The filtrate was evaporated under vacuum and the resulting residue was distilled at reduced pressure to give a colorless liquid (58.0 g, 88 %) of phenylsulfur chlorotetrafluoride: b.p. 80°C/20 mmHg; ^1H NMR (CD_3CN) 7.79-7.75 (m, 2H, aromatic), 7.53-7.49 (m, 3H, aromatic); ^{19}F NMR (CD_3CN) 136.7 (s, SF_4Cl). The NMR analysis showed phenylsulfur chlorotetrafluoride obtained is a trans isomer.

[00111] (Process II) A 100 mL fluoropolymer (TEFLON®-PFA) vessel was charged with $PhSF_4Cl$ (44 g, 0.2mol) and dry ZnF_2 (12.3 g, 0.12 mol) in a dry box filled with N_2. The vessel was then equipped with a condenser made of fluoropolymer and a balloon filled with N_2. The reaction mixture was slowly heated to 120°C over a period of one hour. The reaction mixture changed from colorless to yellow, pink, and then eventually green. The reaction mixture was stirred at 120°C for 20 h. After being cooled to room temperature, about 50 mL of pentane was added to the reaction mixture. The mixture was filtered to remove all insoluble solid to give a yellow solution, which was concentrated. The resulting residue was distilled at reduced pressure to give 30.6 g (75%) of phenylsulfur pentafluoride; b.p. 70-71°C/120 mmHg; ^1H NMR($CDCl_3$) 7.77-7.74 (m, 2H, aromatic), 7.60-7.40 (m, 3H, aromatic); ^{19}F NMR ($CDCl_3$) 85.20-84.13 (m, 1F, SF_5), 62.91 (d, 4F, SF_5).

Examples 2-10. Synthesis of arylsulfur pentafluorides (I) from aryl sulfur compounds (IIa)



R=a substituted group IIa IV I

[00112] Substituted arylsulfur pentafluorides (I) were synthesized from the corresponding aryl sulfur compounds (IIa) by the similar procedure as in Example 1. Table 3 shows the synthesis of the substituted arylsulfur pentafluorides. Table 3 also shows the starting materials and other chemicals necessary for the Processes I and II, solvents, reaction conditions, and the results, together with those of Example 1. FC-72 (Fluorinert®) was used as a solvent in Process II in Examples 9 and 10. The Fluorinert® FC-72 was a perfluorinated organic compound having a boiling point of 56 °C, which was a product made by 3M Company.

Table 3: Production of Arylsulfur pentafluorides (I) from Aryl sulfur compounds (IIa)

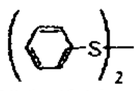
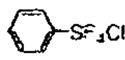
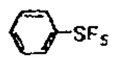
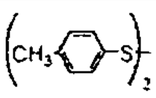
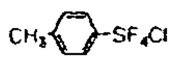
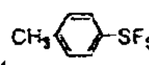
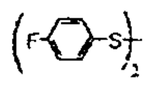
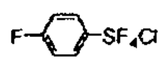
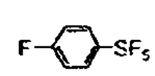
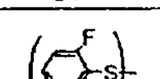
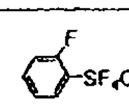
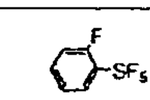
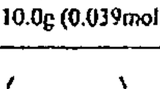
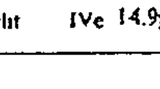
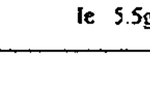
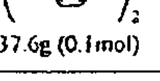
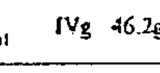
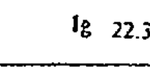
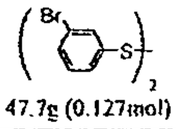
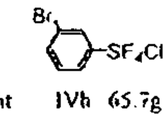
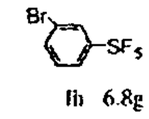
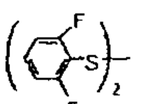
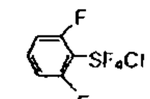
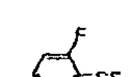
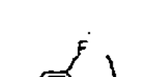
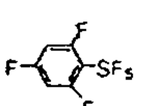
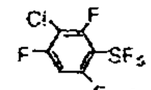
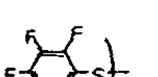
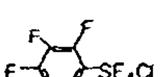
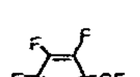
Ex.	Process I							Process II					
	(IIa)	Halogen	(III)	Solvent	Conditions	(IV)	Yield	Amount of (IV)	Fluoride source	Solv.	Conditions	(I)	Yield
1	 33.0g (0.15mol)	Cl_2 ~1.2mol	KF 140g (2.4mol)	CH_3CN 300mL	0~5°C ~9.5 h	 IVa 58g	88%	44g (0.2mol)	ZnF_2 12.5g (0.12mol)	non	120°C 20 h	 Ia 30.6g	75%
2	 123g (05mol)	Cl_2 0.73mol	KF 464g (8mol)	CH_3CN 1L	0°C 10.5h	 IVb 170g	73%	32g (137mmol)	ZnF_2 8.47g (82mmol)	non	90°C overnight	 Ib 21.1g	71%
3	 10.0g (0.039mol)	Cl_2 0.28mol	KF 36 g (0.63mol)	CH_3CN 100mL	0~5°C 2.5h and r.t. overnight	 IVd 12.5g	67%	10g (42mmol)	ZnF_2 2.6g (25mmol)	non	120°C 16 h	 Id 5.8g	62%
4	 10.0g (0.039mol)	Cl_2 0.31mol	KF 36.5g (0.63mol)	CH_3CN 100mL	0~5°C 1.8h and r.t. overnight	 IVe 14.9g	80%	10g (42mmol)	ZnF_2 2.59g (25mmol)	non	120°C 15 h	 Ie 5.5g	59%
5	 37.6g (0.1mol)	Cl_2 0.72mol	KF 94g (1.6mol)	CH_3CN 200mL	0~5°C 4.5h and r.t. overnight	 IVg 46.2g	77%	30g (100mmol)	ZnF_2 6.18g (60mmol)	heptane 20mL	reflux 17 h	 Ig 22.3g	79%
6	 47.7g (0.127mol)	Cl_2 0.88mol	KF 118g (2.0mol)	CH_3CN 250mL	0~5°C 5.5h and r.t. overnight	 IVh 65.7g	86%	10g (33mmol)	ZnF_2 2.0g (20mmol)	non	120°C 15 h	 Ih 6.8g	78%
7	 30.8g (0.1mol)	Cl_2 0.72mol	KF 94g (1.6mol)	CH_3CN 200mL	0~5°C 4.5h and r.t. overnight	 IVi 32g	60%	26.5g (100mmol)	ZnF_2 6.18g (60mmol)	non	150°C 72 h	 Ii 9.0g	36%

Table 3 (continued)

Ex.	Process I							Process II					
	(IIa)	Halogen	(III)	Solvent	Conditions	(IV)	Yield	Amount of (IV)	Fluoride source	Solv.	Conditions	(I)	Yield
8	 29.1g (0.1mol)	Cl_2 ~1.02mol	CsF 279g (1.83mol)	CH_3CN 200mL	0~5°C 5 h and r.t. overnight	 IVj 42.3g	82%	41.87g (0.16mol)	ZnF_2 18.1g (0.17mol)	non	130°C 4h and 180°C 6h	 Ij 20.0g	52%
9	 22.9g (0.07mol)	Cl_2 ~1.08mol	KF 90g (1.55mol)	CH_3CN 300mL	0~5°C 5h and r.t. overnight	IVl 25.8g	67%	4.09g (14.9mmol)	SbF_5 0.5~0.6mL (~8mmol)	FC-72 20mL	r.t. 2h	 Il  Im 3.19g (total)	60% 20%
10	 26.1g (0.065mol)	Cl_2 ~1 mol	KF 82g (1.41mol)	CH_3CN 300mL	0~5°C 5h and r.t. overnight	 IVn 34.9g	86%	9.47g (30.5mmol)	SbF_5 3.4g (30.5mmol)	FC-72 40mL	r.t. 2h	 In 5.36g	60%

[00113] The properties and spectral data of the products, (IV) and (I), obtained by Examples 2-10 are shown by the following:

[00114] p-Methylphenylsulfur chlorotetrafluoride; b.p. 74-75°C/5 mmHg; ^{1}H NMR (CD_3CN) 7.65 (*d*, 2H, aromatic), 7.29 (*d*, 2H, aromatic), 2.36 (*s*, 3H, CH_3); ^{19}F NMR

(CD_3CN) 137.66 (*s*, SF_4Cl); High resolution mass spectrum; found 235.986234 (34.9%) (calcd for $C_7H_7F_4S^{37}Cl$; 235.986363), found 233.989763 (75.6%) (calcd for $C_7H_7F_4S^{35}Cl$; 233.989313). The NMR shows that p-methylphenylsulfur chlorotetrafluoride obtained is a trans isomer.

[00115] p-Methylphenylsulfur pentafluoride; b.p. 95-96°C/80 mmHg; ^1H NMR ($CDCl_3$) 7.63 (*d*, 2H, aromatic), 7.24 (*d*, 2H, aromatic), 2.40 (*s*, 3H, CH_3); ^{19}F NMR ($CDCl_3$) 86.55-84.96 (*m*, 1F, SF), 63.26 (*d*, 4F, SF_4).

[00116] p-Fluorophenylsulfur chlorotetrafluoride; b.p. 60°C/8 mmHg; ^1H NMR (CD_3CN) 7.85-7.78 (*m*, 2H, aromatic), 7.25-7.15 (*m*, 2H, aromatic); ^{19}F NMR (CD_3CN) 137.6 (*s*, SF_4Cl), -108.3 (*s*, CF); High resolution mass spectrum; found 239.961355 (37.4%) (calcd for $C_6H_4F_5S^{37}Cl$; 239.961291), found 237.964201(100%) (calcd for $C_6H_4F_5S^{35}Cl$; 237.964241). The NMR shows that p-fluorophenylsulfur chlorotetrafluoride obtained is a trans isomer.

[00117] p-Fluorophenylsulfur pentafluoride; b.p. 71°C/80 mmHg; ^1H NMR ($CDCl_3$) 7.80-7.73 (*m*, 2H, aromatic), 7.17-7.09 (*m*, 2H, aromatic); ^{19}F NMR ($CDCl_3$) 87.78-83.17 (*m*, 1F, SF), 63.81 (*d*, 4F, SF_4), -107.06 (*s*, 1F, CF); GC-MS m/z 222 (M^+).

[00118] o-Fluorophenylsulfur chlorotetrafluoride; b.p. 96-97°C/20 mmHg; ^1H NMR (CD_3CN) 7.77-7.72 (*m*, 1H, aromatic), 7.60-7.40 (*m*, 1H, aromatic), 7.25-7.10 (*m*, 2H, aromatic); ^{19}F NMR (CD_3CN) 140.9 (*d*, SF_4Cl), -107.6 (*s*, CF); High resolution mass spectrum; found 239.961474 (25.4%) (calcd for $C_6H_4F_5S^{37}Cl$; 239.961291), found 237.964375 (69.8%) (calcd for $C_6H_4F_5S^{35}Cl$; 237.964241). The NMR shows that o-fluorophenylsulfur chlorotetrafluoride obtained is a trans isomer.

[00119] o-Fluorophenylsulfur pentafluoride; b.p. 91-94°C/120 mmHg; ^1H NMR ($CDCl_3$) 7.78-7.73 (*m*, 1H, aromatic), 7.55-7.48 (*m*, 1H, aromatic), 7.27-7.17 (*m*, 2H, aromatic); ^{19}F NMR ($CDCl_3$) 82.38-81.00 (*m*, 1F, SF), 68.10 (*dd*, 4F, SF_4), -108.07-(-108.35) (*m*, 1F, CF).

[00120] p-Bromophenylsulfur chlorotetrafluoride (X); m.p. 58-59 °C; ^1H NMR (CD_3CN) δ 7.67 (s, 4H, aromatic); ^{19}F NMR (CD_3CN) δ 136.56 (s, SF_4Cl); High resolution mass spectrum; found 301.877066 (16.5%) (calcd for $C_6H_4{}^{81}Br{}^{37}ClF_4S$; 301.879178), found 299.880655 (76.6%) (calcd for $C_6H_4{}^{81}Br{}^{35}ClF_4S$; 299.881224 and calcd for $C_6H_4{}^{79}Br{}^{37}ClF_4S$; 299.882128), found 297.882761 (77.4%) (calcd for $C_6H_4{}^{79}Br{}^{35}ClF_4S$; 297.884174). Elemental analysis; calcd for $C_6H_4BrClF_4S$; C, 24.06%; H, 1.35%; found, C, 24.37%; H,

1.54%. The NMR showed that p-bromophenylsulfur chlorotetrafluoride was obtained as a trans isomer.

[00121] p-Bromophenylsulfur pentafluoride; b.p. 77-78°C/10 mmHg; ^{1}H NMR ($CDCl_3$) 7.63 (*s*, 4H, aromatic); ^{19}F NMR ($CDCl_3$) 84.13-82.53 (*m*, 1F, SF), 63.11 (*d*, 4F, SF_4).

[00122] m-Bromophenylsulfur chlorotetrafluoride; b.p. 57-59°C/0.8 mmHg; ^{1}H NMR (CD_3CN) 7.90-7.88 (*m*, 1H, aromatic), 7.70-7.50 (*m*, 2H, aromatic), 7.40-7.30 (*m*, 1H, aromatic); ^{19}F NMR (CD_3CN) 136.74 (*s*, SF_4Cl). High resolution mass spectrum; found 301.878031 (29.1%) (calcd for $C_6H_4{}^{81}Br{}^{37}ClF_4S$; 301.879178), found 299.881066 (100%) (calcd for $C_6H_4{}^{81}Br{}^{35}ClF_4S$; 299.881224 and calcd for $C_6H_4{}^{79}Br{}^{37}ClF_4S$; 299.882128), found 297.883275 (77.4%) (calcd for $C_6H_4{}^{79}Br{}^{35}ClF_4S$; 297.884174). The NMR showed that m-bromophenylsulfur chlorotetrafluoride obtained was a trans isomer.

[00123] m-Bromophenylsulfur pentafluoride; b.p. 69-70°C/10 mmHg; ^{1}H NMR ($CDCl_3$) 7.91 (*t*, 1H, aromatic), 7.72-7.64 (m, 2H, aromatic), 7.35 (*t*, 1H, aromatic); ^{19}F NMR ($CDCl_3$) 83.55-82.47 (*m*, 1F, SF), 63.13 (*d*, 4F, SF_4).

[00124] p-Nitrophenylsulfur chlorotetrafluoride; m.p. 130-131 °C; ^{1}H NMR (CD_3CN) 8.29 (*d*, J=7.8 Hz, 2H, aromatic), 8.02 (*d*, J=7.8 Hz, 2H, aromatic); ^{19}F NMR (CD_3CN) 134.96 (*s*, SF_4Cl); High resolution mass spectrum; found 266.956490 (38.4%) (calcd for $C_6H_4{}^{37}ClF_4NO_2S$; 266.955791), found 264.959223 (100%) (calcd for $C_6H_4{}^{35}ClF_4NO_2S$; 264.958741). Elemental analysis; calcd for $C_6H_4ClF_4NO_2S$; C, 27.13%; H, 1.52%; N, 5.27%; found, C, 27.16%; H, 1.74%; N, 4.91%. The NMR shows that p-nitrophenylsulfur chlorotetrafluoride obtained is a trans isomer.

[00125] p-Nitrophenylsulfur pentafluoride; b.p. 74-76°C/3 mmHg; ^{1}H NMR ($CDCl_3$) 8.36-8.30 (*m*, 2H, aromatic), 7.99-7.95 (*m*, 2H, aromatic); ^{19}F NMR ($CDCl_3$) 82.32-80.69 (*m*, 1F, SF), 62.76 (*d*, 4F, SF_4).

[00126] 2,6-Difluorophenylsulfur chlorotetrafluoride: The product (b.p. 120-122 °C/95-100mmHg) obtained from Example 8 is a 6:1 mixture of trans- and cis-isomers of 2,6-difluorophenylsulfur chlorotetrafluoride. The trans-isomer was isolated as pure form by crystallization; mp. 47.6-48.3 °C; ^{19}F NMR ($CDCl_3$) δ 143.9 (t, J=26.0 Hz, 4F, SF_4), -104.1 (quintet, J=26.0 Hz, 2F, 2,6-F): ^{1}H NMR ($CDCl_3$) δ 6.97-7.09 (m, 2H, 3,5-H), 7.43-7.55 (m, 1H, 4-H); ^{13}C NMR ($CDCl_3$) δ 157.20 (d, J=262.3 Hz), 133.74 (t, J=11.6 Hz), 130.60 (m), 113.46 (d, J=14.6 Hz); high resolution mass spectrum; found 257.950876 (37.6%) (calcd for $C_6H_3{}^{37}ClF_6S$; 257.951869), found 255.955740 (100%) (calcd for $C_6H_3{}^{35}ClF_6S$; 255.954819);

elemental analysis; calcd for $C_6H_3ClF_6S$; C, 28.08%, H, 1.18%; found; C, 28.24%, H, 1.24%. The cis-isomer was assigned in the following; ^{19}F NMR ($CDCl_3$) δ 158.2 (quartet, J=161.8 Hz, 1F, SF), 121.9 (m, 2F, SF_2), 76.0 (m, 1F, SF). The ^{19}F NMR assignment of aromatic fluorine atoms of the cis-isomer could not be done because of possible overlapping of the peaks of the trans-isomer.

[00127] 2,6-Difluorophenylsulfur pentafluoride: m.p. 40.3-41.1 °C; ^1H NMR ($CDCl_3$) δ 7.51 (*m*, 1H), 7.04 (*m*, 2H); ^{19}F NMR ($CDCl_3$) 82.32-80.69 (*m*, 1F, SF), 62.76 (*d*, 4F, SF_4); high resolution mass spectrum; found 239.984509 (calcd for $C_6H_3F_7S$; 239.984370); elemental analysis, calcd for $C_6H_3F_7S$; C, 30.01%, H, 1.26%; found, C, 30.20%, H, 1.47%.

[00128] 2,4,6-Trifluorophenylsulfur chlorotetrafluoride: trans-isomer; m.p. 55.8-56.7 °C; ^{19}F NMR ($CDCl_3$) δ 144.07 (t, J=26.0 Hz, 4F, SF_4), -99.80 (t, J=26.0 Hz, 2F, o-F), -100.35 (s, 1F, p-F); ^1H NMR ($CDCl_3$) δ 6.79 (t, J=17.5 Hz, m-H); ^{13}C NMR ($CDCl_3$) δ 164.16 (dt, J=164.2 Hz, 15.2 Hz, 4-C), 158.18 (dm, J=260.7 Hz, 2-C), 127.7 (m, 1-C), 102.1 (tm, J=27.8 Hz, 3-C). Elemental analysis; calcd for $C_6H_2ClF_7S$; C, 26.24%; H, 0.73%; found, C, 26.23%; H, 1.01%. The NMR shows that 2,4,6-trifluorophenylsulfur chlorotetrafluoride obtained is a trans isomer.

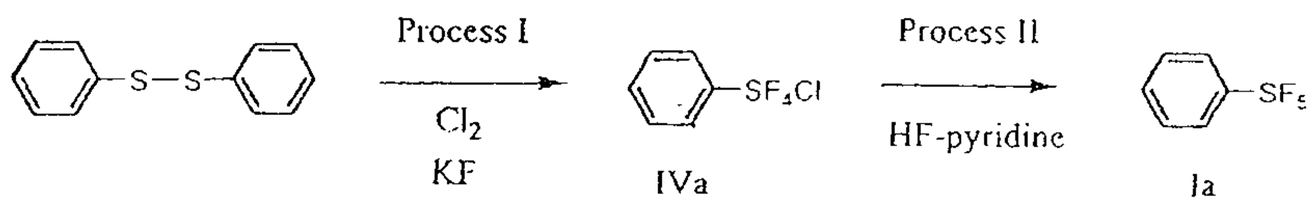
[00129] 2,4,6-Trifluorophenylsulfur pentafluoride and 3-chloro-2,4,6-trifluorophenylsulfur pentafluoride: The product (b.p.~145°C) obtained from Experiment 9 was a 3:1 (molar ratio) mixture of 2,4,6-trifluorophenylsulfur pentafluoride and 3-chloro-2,4,6-trifluorophenylsulfur pentafluoride. These products were identified by NMR and GC-Mass analysis. 2,4,6-Trifluorophenylsulfur pentafluoride: ^{19}F NMR ($CDCl_3$) δ 78.7-75.3 (m, SF), 73.8-72.9 (m, SF_4), -100.6 (m, 4-F), -100.7 (m, 2,6-F) ; ^1H NMR ($CDCl_3$) δ 6.80 (t, J=8.6 Hz, 3,5-H); GC-Mass m/z 258 (M^+). 3-Chloro-2,4,6-trifluorophenylsulfur pentafluoride: ^{19}F NMR ($CDCl_3$) δ 78.7-75.3 (m, SF), 73.8-72.9 (m, SF_4), -101.3 (m, 2 or 6-F), -102.3 (m, 4-F), -102.6 (m, 2 or 6-F); ^1H NMR ($CDCl_3$) δ 6.95 (br.t, J=9.5 Hz, 5-H); GC-Mass m/z 294, 292 (M^+).

[00130] 2,3,4,5,6-Pentafluorophenylsulfur chlorotetrafluoride: The product (b.p. 95-112 °C/100 mmHg) obtained from Experiment 10 was a 1.7:1 mixture of trans and cis isomers of 2,3,4,5,6-pentafluorophenylsulfur chlorotetrafluoride. The isomers were assigned by ^{19}F NMR: The trans isomer; ^{19}F NMR ($CDCl_3$) δ 144.10 (t, J=26.0 Hz, 4F, SF_4), -132.7 (m, 2F, 2,6-F), -146.6 (m, 1F, 4-F), -158.9 (m, 2F, 3,5-F); ^{13}C NMR ($CDCl_3$) δ 143.5 (dm, J=265.2 Hz), 141.7 (dm, J=263.7 Hz), 128.3 (m). The cis isomer; ^{19}F NMR ($CDCl_3$) δ 152.39

(quartet, J=158.9 Hz, 1F, SF), 124.32 (m, 2F, SF_2), 79.4 (m, 1F, SF), -132.7 (m, 2F, 2,6-F), -146.6 (m, 1F, 4-F), -158.9 (m, 2F, 3,5-F). High resolution mass spectrum of a 1.7:1 mixture of the trans and cis isomers; found 311.923124 (15.5%) (calcd for $C_6{}^{37}ClF_9S$; 311.923604), found 309.926404 (43.1%) (calcd for $C_6{}^{35}ClF_9S$; 309.926554).

[00131] 2,3,4,5,6-Pentafluorophenylsulfur pentafluoride: b.p. 135-137 °C; ^{19}F NMR ($CDCl_3$) δ 74.8 (m, 5F, SF_5), -133.4 (m, 2F, 2,6-F), -146.2 (m, 1F, 4-F), -158.6 (m, 2F, 3,5-F); ^{13}C NMR ($CDCl_3$) δ 143.6 (dm, J=262.2 Hz), 137.9 (dm, J=253.6 Hz), 126.7 (m). High resolution mass spectrum; found 293.956492 (calcd for $C_6F_{10}S$; 293.956104).

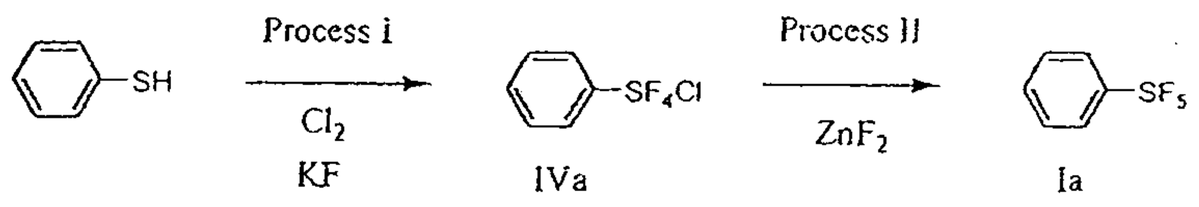
Example 11. Synthesis of phenylsulfur pentafluoride from diphenyl disulfide with a mixture of hydrogen fluoride and pyridine as a fluoride source in Process II



[00132] (Process I) Phenylsulfur chlorotetrafluoride was prepared in a high yield in the same manner as in Process I in Example 1.

[00133] (Process II) A reaction vessel made of fluoropolymer was charged with 341 mg (1.54 mmol) of trans-phenylsulfur chlorotetrafluoride, and 0.5 mL of a mixture of about 70wt% hydrogen fluoride and about 30wt% pyridine was added at room temperature. The reaction mixture was stirred at room temperature for 1 hour and heated at 50 °C for 3 hours. After the reaction, the reaction mixture was cooled to room temperature. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 93% yield.

Example 12. Synthesis of phenylsulfur pentafluoride from thiophenol as an aryl sulfur compound of formula (IIb)

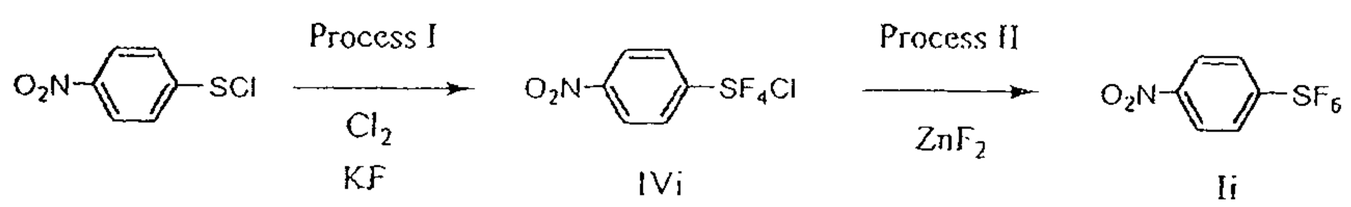


[00134] (Process I) Chlorine (Cl_2) was passed with a flow rate of 27 mL/min into a stirred mixture of 10.0 g (90.8 mmol) of thiophenol and 47.5 g (0.817 mol) of dry KF in 100mL of dry acetonitrile at 6~10°C. Chlorine was passed for 3.7 h and the total amount of chlorine passed was 10.2 L (0.445 mol). After 10 mL of 1,1,2-trichlorotrifluoroethane was

added to the reaction mixture, the reaction mixture was filtered. After removal of the solvent in vacuum, phenylsulfur chlorotetrafluoride (16.6 g, 83%) as a light green-brown liquid was obtained. The physical properties and spectral data of the product are shown in Example 1. The product was a trans isomer.

[00135] (Process II) Phenylsulfur chlorotetrafluoride obtained in Process I above may be allowed to react with ZnF_2 in the same procedure as Process II in Example 1, giving phenylsulfur pentafluoride in good yield.

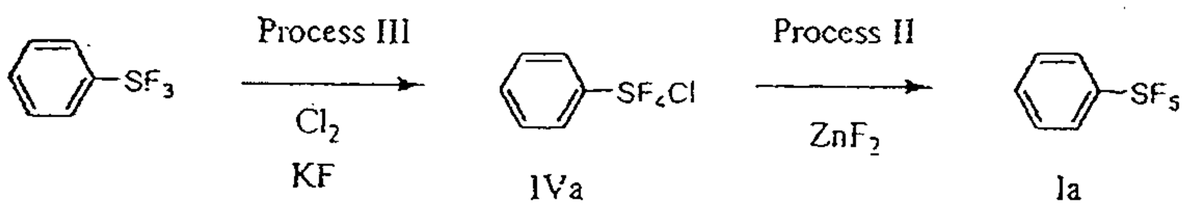
Example 13. Synthesis of p-nitrophenylsulfur pentafluoride from p-nitrobenzenesulfenyl chloride as an aryl sulfur compound of formula (IIb)



[00136] (Process I) Chlorine (Cl_2) was passed with a flow rate of 37 mL/min into a stirred mixture of 5.00 g (26.4 mmol) of p-nitrobenzenesulfenyl chloride and 15.3 g (264 mmol) of dry KF in 40mL of dry acetonitrile at 5~11°C. The total amount of chlorine passed was 2.54 L (113 mmol). After 5 mL of 1,1,2-trichlorotrifluoroethane was added to the reaction mixture, the reaction mixture was filtered. After removal of the solvent in vacuum, p-nitrophenylsulfur chlorotetrafluoride (4.69 g, 76%) as a solid was obtained. The physical properties and spectral data of the product are shown in Example 7. The product was a trans isomer.

[00137] (Process II) p-Nitrophenylsulfur chlorotetrafluoride obtained in Process I above may be allowed to react with ZnF_2 in the same procedure as Process II in Example 7, giving p-nitrophenylsulfur pentafluoride in good yield.

Example 14. Synthesis of phenylsulfur pentafluoride from phenylsulfur trifluoride

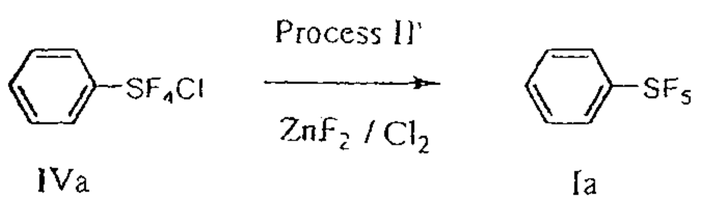


[00138] (Process III) Chlorine (Cl_2) was passed with a flow rate of 34 mL/min into a stirred mixture of 5.00 g (30.1 mmol) of phenylsulfur trifluoride and 8.74 g (150 mmol) of

dry KF in 20 mL of dry acetonitrile at 6~9°C. Chlorine was passed for 43 min and the total amount of chlorine passed was 1.47 L (65.5 mmol). After 3 mL of 1,1,2-trichlorotrifluoroethane was added to the reaction mixture, the reaction mixture was filtered. After removal of the solvent in vacuum, phenylsulfur chlorotetrafluoride (5.62 g, 84%) as a colorless liquid was obtained. The physical properties and spectral data of the product are shown in Example 1. The product was a trans isomer.

[00139] (Process II) Phenylsulfur chlorotetrafluoride obtained in Process III above may be allowed to react with ZnF_2 in the same procedure as Process II in Example 1, giving phenylsulfur pentafluoride in good yield.

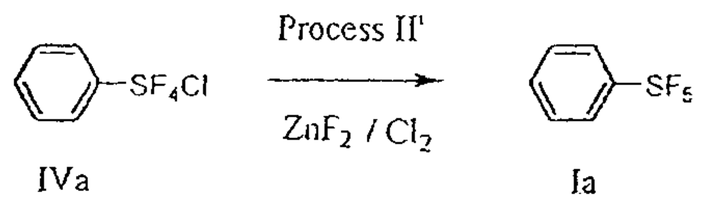
Example 15. Reaction of phenylsulfur chlorotetrafluoride and ZnF_2 under a slow flow of chlorine (presence of halogen)



(Process II') trans-Phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12, or 14. In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (0.045 mol) of trans-$PhSF_4Cl$ and 2.8 g (0.027 mol) of dry ZnF_2. The reaction vessel was brought out from the dry box and connected to the gas flowing system. The reaction mixture was slowly heated to 120°C while Cl_2 gas was added into the reaction vessel at the rate of 4.6 mL/minute. The progress of the reaction was monitored by ^{19}F NMR. After 40 minutes at 120°C, three major compounds (trans-$PhSF_4Cl$, cis-$PhSF_4Cl$, and phenylsulfur pentafluoride ($PhSF_5$)) were detected to be present in the reaction mixture. The mol ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 0.5 : 3.3 : 100. After additional 60 minutes at 120°C, trans- and cis-$PhSF_4Cl$ disappeared and only $PhSF_5$ was detected from ^{19}F NMR. The reaction was completed within 1.7 h at 120°C. After N_2 (5.4 mL/minute) was flowed for 0.5 hour, the examination of the reaction mixture by ^{19}F NMR using benzotrifluoride as a standard showed that phenylsulfur pentafluoride was produced in 92% yield. This experiment showed that the reaction is greatly accelerated by the presence of chlorine and the product is obtained in a

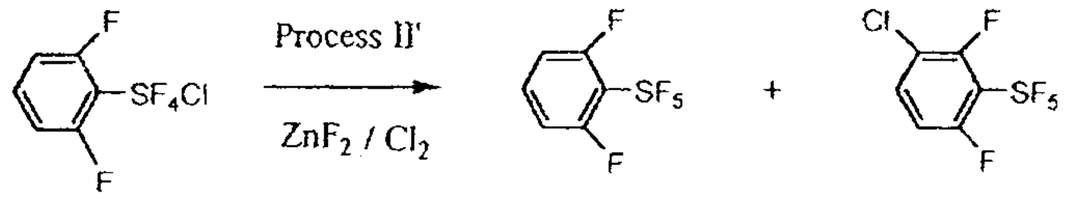
high yield. This experiment also showed that cis-$PhSF_4Cl$ is formed intermediately by the isomerization of trans-$PhSF_4Cl$, and cis-$PhSF_4Cl$ is converted to the product, $PhSF_5$.

Example 16. Reaction of phenylsulfur chlorotetrafluoride and ZnF_2 under a fast flow of chlorine (presence of halogen)



[00140] (Process II') trans-Phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12 or 14. In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (0.045 mol) of trans-$PhSF_4Cl$ and 2.8 g (0.027 mol) of dry ZnF_2. The reaction vessel was brought out from the dry box and connected to the gas flowing system. The reaction mixture was slowly heated to 120°C while Cl_2 gas was added into the reaction vessel at the rate of 23 mL/minute. The progress of the reaction was monitored by ^{19}F NMR. After 45 minutes at 120°C, three major compounds (trans-$PhSF_4Cl$, cis-$PhSF_4Cl$, and phenylsulfur pentafluoride ($PhSF_5$)) were detected to be present in the reaction mixture. The mol ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 18 : 83 : 100. After additional 45 minutes at 120°C, trans- and cis-$PhSF_4Cl$ disappeared and only $PhSF_5$ was detected from ^{19}F NMR. The reaction was completed in about 1.5 h at 120°C. After N_2 (26.9 mL/minute) was flowed for 1 hour, the examination of the reaction mixture by ^{19}F NMR using benzotrifluoride as a standard showed that phenylsulfur pentafluoride was produced in 83% yield. This experiment showed that the reaction is greatly accelerated by the presence of chlorine and the product is obtained in a high yield. This experiment clearly showed that cis-$PhSF_4Cl$ is formed intermediately by the isomerization of trans-$PhSF_4Cl$, and cis-$PhSF_4Cl$ is converted to the product, $PhSF_5$.

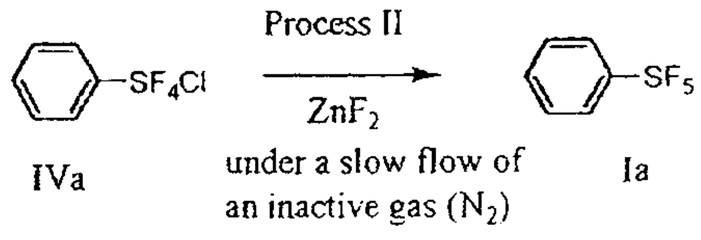
Example 17. Reaction of 2,6-difluorophenylsulfur chlorotetrafluoride and ZnF_2 under a flow of chlorine (presence of halogen)



IVj Ij Ik

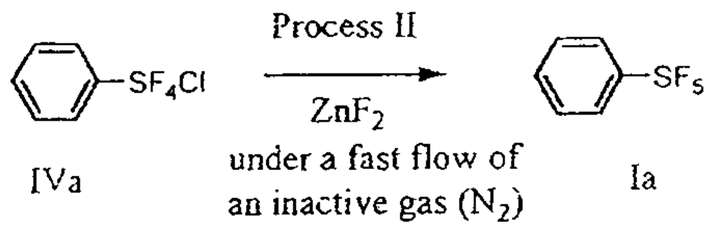
[00141] (Process II') A 6:1 mixture of trans and cis-2,6-difluorophenylsulfur chlorotetrafluoride used for this Process was prepared in high yields by the Process I or III as shown by Examples 8. In a dry box, a 100 mL reaction vessel made of fluoropolymer was charged with 13.03 g (0.126 mol) of dry ZnF_2. The reaction vessel was brought out from the dry box and connected to the gas flowing system. After nitrogen purge, Cl_2 gas started to flow into the reaction vessel at the rate of 15 mL/minute as the reaction vessel was heated to 130-140°C, at which point addition of 32.36 g (0.126 mol) of the mixture of trans- and cis-2,6-difluorophenylsulfur chlorotetrafluoride was started. A total of 32.36 g (0.126 mol) of the mixture of trans- and cis-2,6-difluorophenylsulfur chlorotetrafluoride was added over 1 h. After this, heat and chlorine flow were maintained for an additional 3 hours. At this point, the NMR analysis of the reaction mixture showed that the starting materials (trans- and cis-2,6-difluorophenylsulfur chlorotetrafluoride) were consumed and 2,6-difluorophenylsulfur pentafluoride and 3-chloro-2,6-difluorophenylsulfur pentafluoride were produced in 63:37 molar ratio. The reaction mixture was then extracted with pentane and washed with aqueous sodium carbonate solution. The extract was dried with dry Na_2SO_4, filtered, and concentrated to give a residue which was distilled at reduced pressure to give four fractions of the product in the range of boiling point 75~120 °C at 110 mmHg. The first three fractions (total 15.37g) was a 1:1 mixture (by GC) of 2,6-difluorophenylsulfur pentafluoride and 3-chloro-2,6-difluorophenylsulfur pentafluoride. The final fraction (the fourth fraction, b.p. 112-120 °C/110 mmHg) had 6.22 g of 3-chloro-2,6-difluorophenylsulfur pentafluoride (93% purity, determined by GC). The spectral data of 3-chloro-2,6-difluorophenylsulfur pentafluoride were as follows; ^{19}F NMR ($CDCl_3$) δ 77.9-75.7 (m, 1F, SF), 73.2-72.5 (m, 4F, SF_4), -103.3 (m, 1F), -105.2 (m, 1F); ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 1H), 7.04 (m, 1H); high resolution mass spectrum, found 275.942071 (36.0%) (calcd for $C_6H_2{}^{37}ClF_7S$; 275.942447), found 273.945943 (100%) (calcd for $C_6H_2{}^{35}ClF_7S$; 273.945397). The other product, 2,6-difluorophenylsuflur pentafluoride was identified by the data obtained by Example 8 (Process II).

Example 18. Reaction of phenylsulfur chlorotetrafluoride and ZnF_2 under a slow flow of an inactive gas (nitrogen)



[00142] (Process II) trans-Phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12 or 14. In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (0.045 mol) of trans-$PhSF_4Cl$ and 2.8 g (0.027 mol) of dry ZnF_2. The reaction vessel was brought out from the dry box and connected to the gas flowing system. The reaction mixture was slowly heated to 120°C with N_2 flowing at the rate of 5.4 mL/minute. The reaction mixture changed from colorless to light yellow, to pink, and eventually to brown in about 30 minutes. The reaction mixture was stirred at 120°C with N_2 flowing for 5 hours. After being cooled down to room temperature, the reaction mixture was checked with ^{19}F NMR. Three major compounds (trans-$PhSF_4Cl$, cis-$PhSF_4Cl$ and $PhSF_5$) were present in the reaction mixture. The ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 15 : 20 : 100. $PhCF_3$ (1.0 g) was added to the reaction mixture and the NMR yield of each compound was determined. The yield of trans-$PhSF_4Cl$ was 2.4%, cis-$PhSF_4Cl$ was 14.6 %, and $PhSF_5$ was 67.2 %. The reaction was not complete in 5 h at 120°C. Therefore, this experiment showed that the reaction under the flow of nitrogen was slowed down.

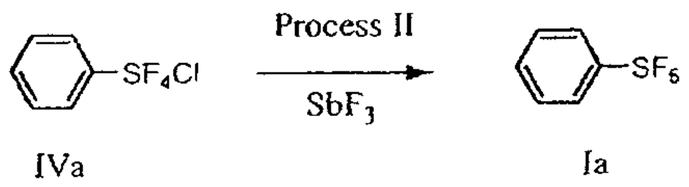
Example 19. Reaction of phenylsulfur chlorotetrafluoride and ZnF_2 under a fast flow of inactive gas (nitrogen)



[00143] (Process II) trans-Phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) used for this Process was prepared in high yields by Process I or III as shown by Examples 1, 11, 12 or 14. In a dry box, a 50 mL reaction vessel made of fluoropolymer was charged with 10.0 g (0.045 mol) of trans-$PhSF_4Cl$ and 2.8 g (0.027 mol) of dry ZnF_2. The reaction vessel was brought out from the dry box and connected to the gas flowing system. The reaction mixture was slowly heated to 120°C with N_2 flowing at a rate of 26.9 mL/minute. The reaction mixture changed from colorless to light yellow, to pink, and eventually to brown in about 30 minutes. The reaction mixture was stirred at 120°C with N_2 flowing for 5 hours. After being

cooled down to room temperature, the reaction mixture was checked with ^{19}F NMR. Three major compounds (trans-$PhSF_4Cl$, cis-$PhSF_4Cl$ and $PhSF_5$) were present in the reaction mixture. The ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 22 : 117 : 100. $PhCF_3$ (2.8g) was added to the reaction mixture and the NMR yield of each compound was determined by ^{19}F NMR. The yield of trans-$PhSF_4Cl$ was 6.7 %, cis-$PhSF_4Cl$ was 42.1 %, and $PhSF_5$ was 38.4 %. The reaction was not complete in 5 h at 120°C and the conversion of $PhSF_4Cl$ to $PhSF_5$ was lower than in Example 18. This reaction showed that the reaction under the fast flow of nitrogen was slowed down more than the reaction under the slow flow of nitrogen. In either case a flow of inactive gas has an inhibitory effect on reaction yield.

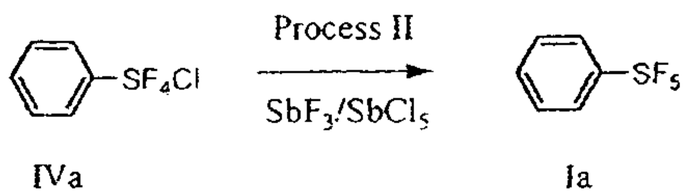
Example 20. Synthesis of phenylsulfur pentafluoride by using SbF_3 as a fluoride source



IVa Ia

[00144] (Process II) trans-Phenylsulfur chlorotetrafluoride used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12, or 14. In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.397 g (2.22 mmol) of dry SbF_3. The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was stirred at 80°C for 5 h. The analysis of the reaction mixture by ^{19}F-NMR technique showed that phenylsulfur pentafluoride was produced in 33% yield.

Example 21. Synthesis of phenylsulfur pentafluoride by using a mixture of SbF_3 (fluoride source) and $SbCl_5$ (fluoride source-activating compound) as a fluoride source

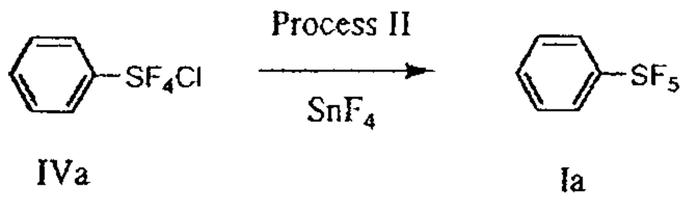


IVa Ia

[00145] (Process II) trans-Phenylsulfur chlorotetrafluoride used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12, or 14. In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride, 0.349 g (2.01 mmol) of SbF_3, a trace amount of $SbCl_5$, and 2 mL of dry hexane. $SbCl_5$ is a fluoride source-activating compound. $SbCl_5$ (strong Lewis acid) can complex with SbF_3 to form $SbF_2(SbFCl_5)$, which can also be made by SbF_2Cl and

$SbFCl_4$ both are fluoride sources usable in this invention. The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was stirred at room temperature for 3 days. The analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 54% yield.

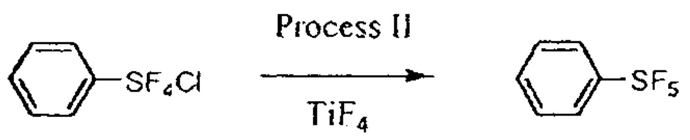
Example 22. Synthesis of phenylsulfur pentafluoride by using SnF_4 as a fluoride source



IVa Ia

[00146] (Process II) trans-Phenylsulfur chlorotetrafluoride used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12, or 14. In a box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.26 g (1.4 mmol) of dry SnF_4. The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was stirred at 80°C for 2 h. The analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 34% yield.

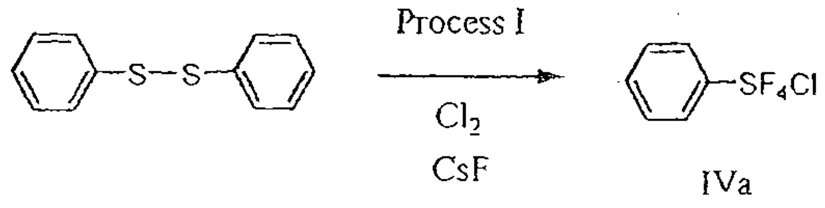
Example 23. Synthesis of phenylsulfur pentafluoride by using TiF_4 as a fluoride source



IVa Ia

[00147] (Process II) trans-Phenylsulfur chlorotetrafluoride used for this Process was prepared in high yields by the Process I or III as shown by Examples 1, 11, 12, or 14. In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.17 g (1.4 mmol) of dry TiF_4. The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was stirred at 80°C for 16 h. The analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 35% yield.

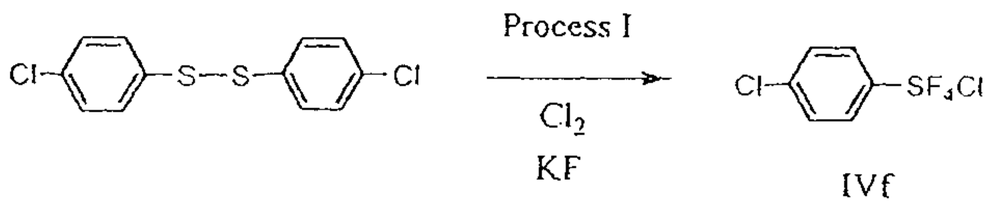
Example 24. Synthesis of phenylsulfur chlorotetrafluoride from diphenyl disulfide



IVa

[00148] (Process I) A 500 mL round bottom flask was charged with diphenyl disulfide (21.8 g, 0.1 mol), dry CsF (243.2 g, 1.6 mol) and 200 mL of dry CH_3CN. The reaction mixture was cooled on an ice/water bath, and bubbled with N_2 (18 mL/min) for 0.5 h. After the N_2 flow was stopped, Cl_2 was bubbled into a reaction mixture at the rate of 63 mL/min for 4 h. The total amount of Cl_2 used was 0.68 mol. The reaction mixture was then warmed to room temperature and stirred overnight. Then, N_2 (18 mL/min) was bubbled through for 2 hours to remove an excess of chlorine. The reaction mixture was filtered with 100 mL of dry hexanes in a dry box. The combined filtrate was evaporated under vacuum, and the residue was distilled at reduced pressure to give a colorless liquid of phenylsulfur chlorotetrafluoride (36.3 g, 83%). The physical properties and spectral data of the product are shown in Example 1. The product was a trans isomer.

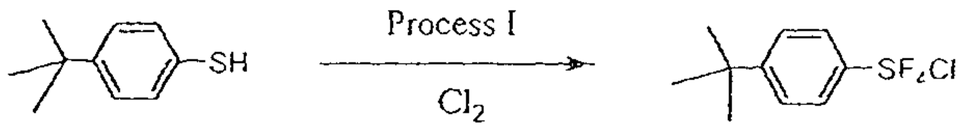
Example 25. Synthesis of p-chlorophenylsulfur chlorotetrafluoride from bis(p-chlorophenyl) disulfide



IVf

[00149] (Process I) Chlorine (Cl_2) was passed with a flow rate of 64 mL/min into a stirred mixture of 25.0 g (87.0 mmol) of bis(p-chlorophenyl) disulfide and 86.0 g (1.48 mol) of dry KF in 200 mL of dry acetonitrile at 5~8°C. Chlorine was passed for 3.5 h and the total amount of chlorine passed was 12.8 L (571 mmol). After that, the reaction mixture was filtered and rinsed with dry hexane. After removal of the solvent in vacuum, p-chlorophenylsulfur chlorotetrafluoride (39.5 g, 88%) as a colorless liquid was obtained; b.p. 65-66 °C/2 mmHg; ^1H NMR ($CDCl_3$) δ 7.38 (*d*, 2H, J=9.1 Hz), 7.65 (*d*, 2H, J=9.1 Hz); ^{19}F NMR ($CDCl_3$) 137.4 (*s*, 4F, SF_4Cl). High resolution mass spectrum; found 257.927507 (13.3%) (calcd for $C_6H_4F_4S^{37}Cl_2$; 257.928790), found 255.930746 (68.9%) (calcd for $C_6H_4F_4S^{37}Cl^{35}Cl$; 255.931740), found 253.933767 (100.0%) (calcd for $C_6H_4F_4S^{35}Cl_2$; 253.934690). The NMR showed that p-chlorophenylsulfur chlorotetrafluoride obtained is a trans isomer.

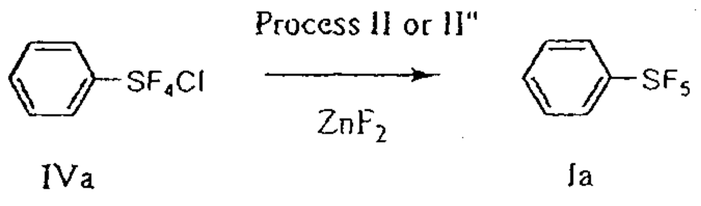
Example 26. Synthesis of p-(tert-butyl)phenylsulfur chlorotetrafluoride from p-(tert-butyl)benzenethiol



IVc

[00150] (Process I) Chlorine (Cl_2) was passed with a flow rate of 35 mL/min into a stirred mixture of 10.0 g (60.2 mmol) of p-(tert-butyl)benzenethiol and 91.6 g (602 mmol) of dry CsF in 150 mL of dry acetonitrile at 5~10°C. Chlorine was passed for 3.5 h and the total amount of chlorine passed was 10.1 L (452 mmol). After that, the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered under dry nitrogen. After removal of the solvent at reduced pressure, the residue was distilled to give 14 g (84%) of p-(tert-butyl)phenylsulfur chlorotetrafluoride; b.p. 98 °C/0.3 mmHg; m.p. 93 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H, $C(CH_3)_3$), 7.43 (d, J=9.2 Hz, 2H, aromatic), 7.64 (d, J=9.2 Hz, 2H, aromatic); ^{19}F NMR δ 138.3 (s, SF_4Cl). High resolution mass spectrum; found 278.034576 (8.8%) (calcd for $C_{10}H_{13}{}^{37}ClF_4S$; 278.033313), found 276.037526 (24.7%) (calcd for $C_{10}H_{13}{}^{35}ClF_4S$; 276.036263). Elemental analysis; Calcd for $C_{10}H_{13}ClF_4S$; C, 43.40%; H, 4.74%. Found; C, 43.69%, H, 4.74%. The NMR showed that p-(t-butyl)phenylsulfur chlorotetrafluoride was obtained as a trans isomer.

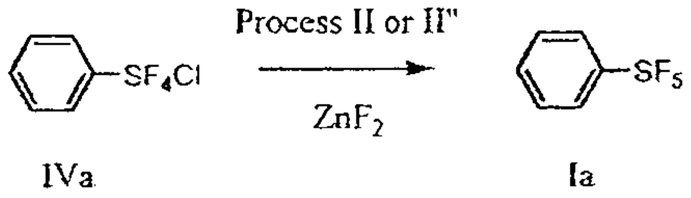
Example 27. Synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride and ZnF_2



IVa Ia

[00151] (Process II or II'') In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.281 g of dry ZnF_2 (solid, mp 872°C, bp 1500°C). The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was heated at 80°C for 20 h. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 85% yield.

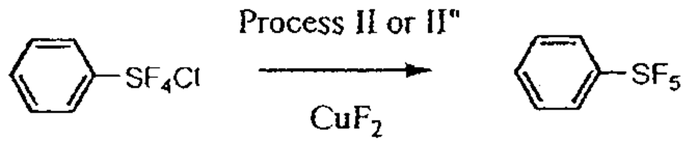
Example 28. Synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride and ZnF_2



IVa Ia

[00152] (Process II or II'') In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.28 g (2.7 mmol) of dry ZnF_2 (solid, mp 872°C, bp 1500°C). The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was heated at 120°C for 4 h. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 88% yield.

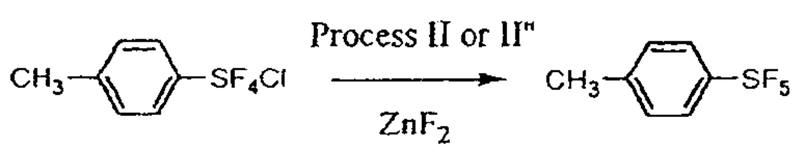
Example 29. Synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride and CuF_2



IVa Ia

[00153] (Process II or II'') In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.54 mmol) of trans-phenylsulfur chlorotetrafluoride and 0.284 g (2.79 mmol) of dry CuF_2 (solid, mp ~785°C). The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was heated at 80°C for 22 h. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was produced in 57% yield.

Example 30. Synthesis of p-methylphenylsulfur pentafluoride from p-methylphenylsulfur chlorotetrafluoride and ZnF_2

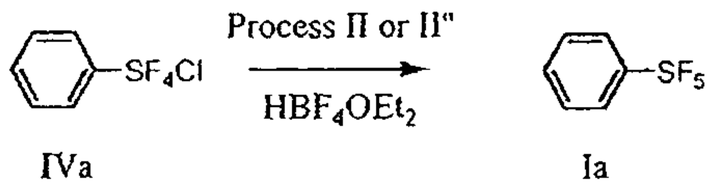


IVb Ib

[00154] (Process II or II'') In a dry box, a reaction vessel made of fluoropolymer was charged with 1.01 g (4.26 mmol) of trans-p-methylphenylsulfur chlorotetrafluoride and 0.266 g (2.57 mmol) of dry ZnF_2 (solid, mp 872°C, bp 1500°C). The reaction vessel was brought out from the dry box and equipped with a balloon filled with N_2. The mixture was heated at

80°C for 16 h. An analysis of the reaction mixture by ^{19}F-NMR showed that p-methylphenylsulfur pentafluoride was produced in 79% yield.

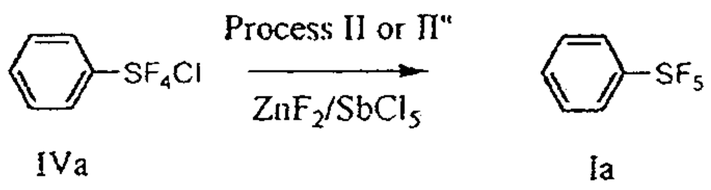
Example 31. Synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride and HBF_4 diethyl etherate



IVa Ia

(Process II or II") In a dry box, a reaction vessel made of fluoropolymer was charged with 1.0 g (4.5 mmol) of trans-phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) and 4.5 mL of dry methylene chloride. The reaction vessel was brought out from the dry box and equipped with a balloon filled with nitrogen. Into the solution, HBF_4 diethyl etherate (liquid) (HBF_4OEt_2) (0.88 g, 0.74 mL, 5.4 mmol) was slowly added. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by ^{19}F NMR. After 7 hours, three major compounds (trans-$PhSF_4Cl$, cis-$PhSF_4Cl$ and $PhSF_5$) were present in the reaction mixture. The ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 156 : 716 : 100. After 21 hours, the ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ changed to 3 : 6 : 100. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride ($PhSF_5$) was produced in 40% yield.

Example 32. Synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride by using a mixture of ZnF_2 (fluoride source) and $SbCl_5$ (fluoride source-activating compound) as a fluoride source

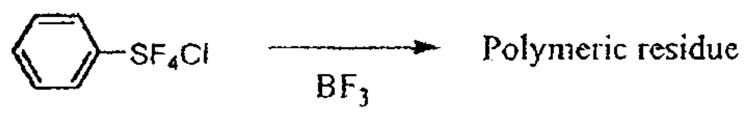


IVa Ia

In a dry box, a reaction vessel made of fluoropolymer was charged with dry heptane (5 mL) and ZnF_2 (solid) (0.84, 8.2 mmol), $SbCl_5$ (liquid) (0.41 g, 0.17 mL, 1.36 mmol) was added into the mixture. To this, trans-phenylsulfur chlorotetrafluoride (trans-$PhSF_4Cl$) (3.0 g, 13.6 mmol) was slowly added. The reaction vessel was brought out from the dry box and equipped with a balloon filled with nitrogen. $SbCl_5$ is a fluoride source-activating compound. $SbCl_5$ (strong Lewis acid) can complex with ZnF_2 to form $ZnF(SbFCl_5)$, which can also be made by ZnFCl and $SbFCl_4$ both are fluoride sources usable in this invention. The reaction

mixture was stirred at room temperature. The progress of the reaction was monitored by ^{19}F NMR. After 10 minutes, the ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ was 385 : 0 : 100. After 90 minutes, the ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ changed to 63 : trace : 100. After 180 minutes, the ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ changed to 34 : trace : 100. After 17 hours, the ratio of trans-$PhSF_4Cl$: cis-$PhSF_4Cl$: $PhSF_5$ changed to 18 : 2 : 100. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride ($PhSF_5$) was produced in 53% yield. A small amount of the starting trans-$PhSF_4Cl$ (9.4 %) remained.

Example 33. Reaction of phenylsulfur chlorotetrafluoride and BF_3 gas (Comparative Example)



IVa

[00155] A reaction vessel made of steel was charged with 1.0 g (4.5 mmol) of trans-phenylsulfur chlorotetrafluoride and cooled on a dry ice-acetone bath. The reaction vessel was evacuated by a vacuum pump and boron trifluoride gas (BF_3; this boiling point is -100°C at 1 atm) was introduced into the reaction vessel till the pressure reached 18 psi. The reaction mixture was then warmed to room temperature and stood for 3 days. During the time, the pressure was increased to 100 psi with additional BF_3 gas. After the reaction, it was found that all the reaction mixture became a solid residue. Phenylsulfur pentafluoride was not detected.

Example 34. Reaction of phenylsuflur chlorotetrafluoride and BF_3 gas in methylene chloride (Comparative Example)

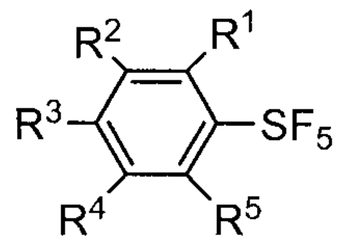
[00156] A reaction vessel made of steel was charged with 1.42 g (6.44 mmol) of trans-phenylsulfur chlorotetrafluoride and 6.4 mL of dry methylene chloride and cooled to about -100°C by using a liquid nitrogen bath. The reaction vessel was evacuated by a vacuum pump and BF_3 gas (boiling point is -100°C at 1 atm) was introduced into the reaction vessel till the pressure reached 80 psi. The reaction mixture was warmed to room temperature and stood for 5 h. During this time, the pressure was increased to 100 psi with additional BF_3 gas. An analysis of the reaction mixture by ^{19}F-NMR showed that phenylsulfur pentafluoride was formed in 28% yield.

[00157] Examples 33 and 34 show that as Ou et al. reported, it was found that, when boron trifluoride (boiling point -100°C at 1 atm) was flowed through a solution of phenylsulfur chlorotetrafluoride in a deuterium methylene chloride, phenylsulfur chlorotetrafluoride was slowly transferred to phenylsulfur pentafluoride (see Can. J. Chem., Vol. 75, pp.1878-1884). As shown herein, however, the yield was very low or the desired product was not obtained because an undesired polymerization occurred. Examples 33 and 34 show the utility of the present invention over the conventional art production method using a fluoride gas such as boron trifluoride whose boiling point is -100°C at 1 atm. The present invention preferably uses fluoride liquids or solids at least at 0°C and at 1 atm, as compared to a gaseous reactant. A liquid or solid is preferable because it is easy to handle and reacts more completely than a gaseous reactant. Also, the reactant of Ou et al., although shown to react at atmospheric pressure, would require high pressure to proceed at an appreciable rate with a necessary and minimum amount of the reactant.

[00158] While the invention has been particularly shown and described with reference to a number of embodiments, it would be understood by those skilled in the art that changes in the form and details may be made to the various embodiments disclosed herein without departing from the scope of the invention and that the various embodiments disclosed herein are not intended to act as limitations on the scope of the claims.

What is claimed is:

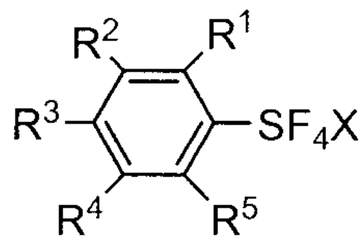
1. A process for preparing an arylsulfur pentafluoride having a formula (I):



---------- (I)

the process comprising:

reacting an arylsulfur halotetrafluoride having a formula (IV);



---------- (IV)

with a fluoride source, wherein the fluoride source is a solid or liquid having a boiling point of approximately 0°C or more at 1 atm, to form the arylsulfur pentafluoride;

in which: R^1, R^2, R^3, R^4, and R^5 each is independently a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group having 1 to 18 carbon atoms, a substituted or unsubstituted aryl group having 6 to 30 carbon atoms, a nitro group, a cyano group, a substituted or unsubstituted alkanesulfonyl group having 1 to 18 carbon atoms, a substituted or unsubstituted arenesulfonyl group having 6 to 30 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 18 carbon atoms, a substituted or unsubstituted aryloxy group having 6 to 30 carbon atoms, a substituted or unsubstituted acyloxy group having from 1 to 18 carbon atoms, a substituted or unsubstituted alkanesulfonyloxy group having from 1 to 18 carbon atoms, a substituted or unsubstituted arenesulfonyloxy group having from 6 to 30 carbon atoms, a substituted or unsubstituted alkoxycarbonyl group having 2 to 18 carbon atoms, a substituted or unsubstituted aryloxycarbonyl group having 7 to 30 carbon atoms, a substituted carbamoyl group having 2 to 18 carbon atoms, a substituted amino group having 1 to 18 carbon atoms, and a SF_5 group;

and

X is a chlorine atom, a bromine atom, or an iodine atom.

2. The process of claim 1 wherein the fluoride source whose boiling point at 1 atm is 0°C or more is at least one member selected from a group consisting of fluorides of typical

elements in the Periodic Table, fluorides of transition elements in the Periodic Table, and mixture or compounds between or among these fluorides of typical elements and/or transition elements, and mixtures, salts, or complexes of these fluorides with organic molecules.