

METHOD FOR PREPARING A SALT AND A SALT PREPARED BY THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a method for preparing a salt, and a salt prepared by the method. More particularly, the invention relates to a method for preparing a salt, by which a salt that is an intermediate mainly used in the production
10 of acid generators or the like, can be synthesized in large quantities at high yields through simplified preparation processes, and a salt prepared by the method.

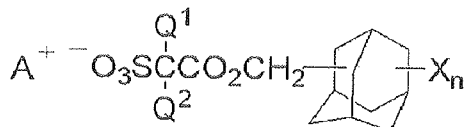
2. Description of the Related Art

As generations pass by, there has been a demand for
15 higher resolution photoresists in the field of fine processing of semiconductors or the like using photolithography. Chemically amplified type photoresist compositions that have been developed in response to such a demand, contain acid generators. In order to produce a
20 resist having increased resolution and desired properties, various types of acid generators have been invented so far.

For example, Japanese Open-Laid Patent Application No. 2006-257078 (hereinafter, referred to as "Patent Document 1") shows an acid generator represented by the following

formula (A):

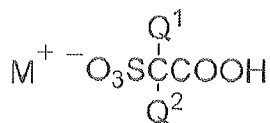
[Formula A]



wherein Q^1 and Q^2 each independently represent a fluorine
5 atom or a perfluoroalkyl group having 1 to 6 carbon atoms; X
represents -OH or -Y-OH; Y represents a linear or branched
alkylene group having 1 to 6 carbon atoms; n represents an
integer from 1 to 9; and A^+ represents an organic counterion.

The Patent Document 1 also discloses, as an
10 intermediate for the production of the acid generator, for
example, an organic compound represented by the following
formula (B):

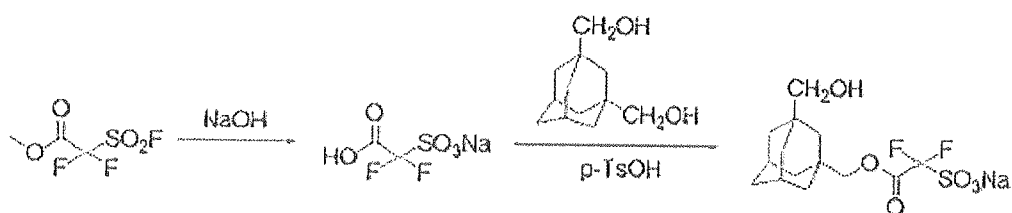
[Formula B]



15 wherein Q^1 and Q^2 each independently represent a fluorine
atom or a perfluoroalkyl group having 1 to 6 carbon atoms;
and M represents Li, Na, K or Ag.

In the Examples of the Patent Document 1, the following
reaction scheme (A) for the synthesis of the compound of
20 formula (A) from the compound of formula (B) is shown.

[Reaction Scheme A]



Specifically, the reaction scheme which is intended to obtain the compound represented by the formula (A), discloses a first step of hydrolyzing the compound represented by the formula (B) with sodium hydroxide to obtain a carboxylic acid compound in an aqueous solution form; and a second step of subjecting the carboxylic acid compound in an aqueous solution form to an esterification reaction.

However, the second step of esterifying the carboxylic acid compound in an aqueous solution state, which is the reaction result of the first step, particularly has a problem of low yield.

On the other hand, Korean Unexamined Patent Application No. 10-2008-0099784 (hereinafter, referred to as "Patent Document 2") discloses inventions related to crystals of an organic compound and a method for production thereof, and the document discloses a method for producing with high efficiency a carboxylic acid compound that is the resultant product of the first step reaction of the reaction scheme A shown above, which method includes a suspension preparation process of supplying an aqueous solution containing an

organic compound to an organic solvent, micronizing the droplets of the aqueous solution to prepare a suspension; and a crystallization process of azeotropically distilling the water from the aqueous solution of the suspension with
5 an organic solvent to crystallize out the crystals of the organic compound.

As such, various attempts have been made to develop a method for preparing a salt with a high yield.

10 SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method for preparing a salt with a high yield, by reducing purification processes and simplifying the reaction steps as compared with the existing
15 methods. Specifically, the method of the present invention involves using a reaction utilizing an alcohol and an amine instead of an aqueous solution of an inorganic base, to obtain a salt.

It is another object of the present invention to
20 provide a salt prepared by the method for preparing a salt described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ^1H -NMR spectrum of the compound B1 produced
25 according to Example 1 of the present invention;

Fig. 2 is a ^1H -NMR spectrum of the compound B2 produced according to Example 1 of the present invention; and

Fig. 3 is a ^{19}F -NMR spectrum of the compound B2 produced according to Example 1 of the present invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be described in detail so that those having ordinary skill in the art to which the present invention is pertained may easily carry
10 out the invention. However, it will be apparent to those skilled in the art that the present invention definitely includes various modifications and modifications, and the present invention is not intended to be limited to the exemplary embodiments explained herein.

15 All of the compounds or substituents as used herein may be unsubstituted or substituted, unless stated otherwise. Here, the term "substituted" means that a hydrogen atom of the compound or substituent is substituted by any one selected from the group consisting a halogen atom, a
20 hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a perfluoroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an alkoxy group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, derivatives thereof and
25 combinations thereof.

Unless stated otherwise, the "halogen atom" as used herein means any one atom selected from the group consisting of fluorine, chlorine, bromine and iodine.

Unless stated otherwise, the "heterocycloalkyl group" or "heteroaryl group" as used herein means a "cycloalkyl group" or "aryl group" containing 1 to 3 heteroatoms selected from the group consisting of nitrogen (N), oxygen (O), sulfur (S) and phosphorus (P) within one ring, with the other atoms in the ring being carbon atoms.

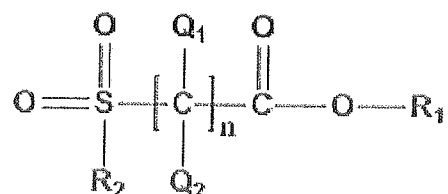
Unless stated otherwise, the "alkyl group" as used herein means a linear or branched alkyl group having 1 to 30 carbon atoms; the "cycloalkyl group" as used herein means a cycloalkyl group having 3 to 30 carbon atoms; the "heterocycloalkyl group" as used herein means a heterocycloalkyl group having 2 to 30 carbon atoms; and the "aryl group" means an aryl group having 6 to 30 carbon atoms. The "alkylene group" as used herein means a linear or branched alkylene group having 1 to 30 carbon atoms; the "cycloalkylene group" as used herein means a cycloalkylene group having 3 to 30 carbon atoms; the "heterocycloalkylene group" as used herein means a heterocycloalkylene group having 2 to 30 carbon atoms; and the "arylene group" as used herein means an arylene group having 6 to 30 carbon atoms.

According to an embodiment of the present invention, there is provided a method for preparing a salt,

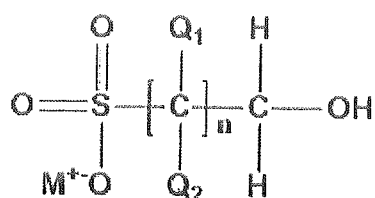
in which a salt can be produced with a high yield through reduced reaction steps and simplified production processes. Hereinafter, the method for preparing a salt will be explained.

5 The method for preparing a salt includes a first step of reacting a compound represented by the following formula (1) with an alcohol and an amine to obtain an ammonium salt; and a second step of reacting the obtained ammonium salt with a reducing agent and an inorganic base to
10 obtain a compound represented by the following formula (2).

[Formula 1]



[Formula 2]



15 wherein in the formulas (1) and (2),

R₁ and R₂ each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a

heterocycloalkyl group, an aryl group and a heteroaryl group;

Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom
5 and a perfluoroalkyl group;

M represents any one selected from the group consisting of lithium (Li), sodium (Na), potassium (K) and silver (Ag); and

n is an integer from 1 to 10.

10 In regard to Q₁ and Q₂, the halogen atom may be a fluorine atom.

First, in order to selectively substitute only R₂ of the compound represented by the formula (1), the compound represented by the formula (1) is reacted with an alcohol
15 and an amine in organic solvent, instead of an aqueous solution of an inorganic base.

The alcohol may be a compound represented by the following formula (3):

[Formula 3]

20 R₃OH

wherein R₃ represents any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an alkoxy group, an aryl group and a heteroaryl group.

25 Specifically, the alcohol may be any one selected from

the group consisting of methanol, ethanol, propanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, oxobutyl alcohol, undecyl alcohol, hydroxydecyl alcohol, heptyl alcohol, 2-methyl-1-pentyl
5 alcohol, allyl alcohol, ethoxycarbonylmethyl alcohol, methoxyethyl alcohol, 1-methoxy-2-propyl alcohol, benzyl alcohol, phenethyl alcohol, cyclohexyl alcohol, menthyl alcohol, tetrahydrofurfuryl alcohol, tetrahydropyranyl alcohol, cyanobutyl alcohol, 4-hydroxy-2-butanone and
10 combinations thereof, but the present invention is not intended to be limited to these.

The amine is an organic amine compound selected from nitrogen-containing compounds, and the amine may be any one selected from the group consisting of a primary amine, a
15 secondary amine, a tertiary amine and combinations thereof, or may be a tertiary amine represented by the following formula (4):

[Formula 4]



20 wherein R_4 to R_6 each independently represent any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroalkyl group; and

when R_5 and R_6 are alkyl groups, they may be linked
25 together to form a hydrocarbon ring.

Specifically, for example, diethylamine, trimethylamine, triethylamine, N,N-diisopropylethylamine, diethylisopropylamine, pyridine, 1-methylpiperidine and the like may be preferably used as the amine, but the present
5 invention is not intended to be limited to these.

The organic solvent may be any organic solvent that is generally used in the related art, and for example, ether, dichloromethane, chloroform, dichloroethane, acetonitrile, toluene and the like may be preferably used, but the present
10 invention is not intended to be limited to these.

In the first step, the compound represented by the formula (1) is dissolved in the organic solvent as mentioned above, and the alcohol is added dropwise to the solution. The mixture is then subjected to stirring. The stirring
15 temperature is preferably from 0 to 60°C, and more preferably from 10 to 30°C. The stirring time is preferably from 10 minutes to 2 hours, and more preferably from 30 minutes to 1 hour.

If the stirring temperature is lower than 0°C, the rate
20 of reaction is low, and if the stirring temperature is higher than 60°C, there may be a problem of heat generation. Furthermore, if the stirring time is shorter than 10 minutes, unreacted substances may remain behind, and if the stirring time exceeds 2 hours, there may be a problem of reverse
25 reaction.

After the mixture of the compound represented by the formula (1) and the alcohol is stirred, the amine is added dropwise thereto, and the mixture is heated to reflux. Subsequently, it is checked whether an ammonium salt, which
5 is a reaction intermediate substance, has been obtained, and the reaction solution is concentrated. The reflux can be carried out at 40 to 150°C for 8 to 20 hours, and preferably for 10 to 14 hours. If the reflux temperature exceeds 150°C, there arises a problem that the yield may be low due to the
10 low boiling point (b.p.) of the product, and if the reflux temperature is below 40°C, there may be a problem that unreacted substances remain behind.

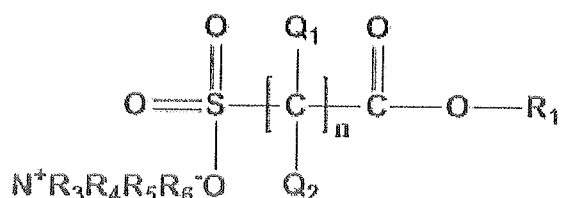
The contents of the compound represented by the formula (1), organic solvent, alcohol and amine can be appropriately
15 regulated according to the reaction conditions. The amine is preferably used at a molar ratio of 1 to 10, and more preferably at molar ratio of 2 to 5, with respect to the compound represented by the formula (1). The alcohol is preferably used at a molar ratio of 1 to 10, and more
20 preferably at a molar ratio of 1 to 5, with respect to the compound represented by the formula (1).

Since the first step utilizes an organic solvent as the reaction solvent, instead of the aqueous solution of an inorganic base that is used in the related art, the
25 solubility of the reaction intermediate substance is

enhanced during the purification process, hydrolysis of the carboxylic acid ester is prevented, and the problem that in the case of separating the reaction intermediate substance in an aqueous solution phase, the reaction intermediate substance adheres to the reaction vessel, thereby markedly reducing the yield, can be overcome.

When the alcohol is the compound represented by the formula (3), and the amine is the compound represented by the formula (4), the ammonium salt may be a compound represented by the following formula (5):

[Formula 5]



wherein R_1 represents any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

Q_1 and Q_2 each independently represents any one selected from the group consisting of a hydrogen atom, a halogen atom and a perfluoroalkyl group;

R_3 represents any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl

group, an alkoxy group, an aryl group and a heteroaryl group;

R₄ to R₆ each independently represent any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

when R₅ and R₆ are alkyl groups, they may be linked together to form a hydrocarbon ring; and

n is an integer from 1 to 10.

10 In Q₁ and Q₂, the halogen atom may be a fluorine atom.

The reaction concentrate is dissolved directly in a solvent without purification, and then a reducing agent and an inorganic base are added to the solution dissolving the reaction concentrate. Then, the compound represented by the formula (2) can be produced.

First, the reaction concentrate is dissolved in an alcoholic solvent such as tetrahydrofuran, methanol, ethanol or propanol, and in an ice bath, the reducing agent is slowly added dropwise to the solution.

20 The reducing agent is preferably any one selected from the group consisting of (CH₂)₄O (tetrahydrofuran, THF), NaBH₄, LiAlH₄, BH₃-THF, NaBH₄-AlCl₃, NaBH₄-LiCl, LiAl(OMe)₃ and combinations thereof, but the present invention is not intended to be limited to these.

25 After the dropwise addition of the reducing agent, when

the reaction is completed, the solvent is removed. The inorganic base is added to the reaction solution from which the solvent has been removed, and then the mixture was stirred, to thereby obtain the sulfonium salt represented by the formula (2).

As for the inorganic base, any salt formed from any one cation selected from the group consisting of alkali metals and alkaline earth metals, and any one anion selected from the group consisting of a sulfate ion, a nitrate ion, a chloride ion, a bromide ion, an iodide ion and a thiocyanate ion, can be used, and preferably, use can be made of a compound represented by the formula: MOH. Here, M is any one selected from the group consisting of Li, Na, K and Ag. The inorganic base may also be used after being dissolved in an aqueous solution.

The stirring may be carried out at 40 to 100°C for 2 to 10 hours. If the stirring temperature is below 40°C, there may be problems in the rate of reaction and the remaining of unreacted substances. If the stirring temperature exceeds 100°C, there arises a problem that the yield may be decreased due to the lowered boiling point (b.p.) of the alcoholic solvent. If the stirring time is shorter than 2 hours, there may be a problem that unreacted substances remain behind, and if the stirring time exceeds 10 hours, there may be a problem that the product undergoes

discoloration.

The contents of the reducing agent and the inorganic base can be appropriately regulated according to the reaction conditions. The reducing agent is preferably used
5 at a molar ratio of 1 to 5 with respect to the compound represented by the formula (1), so that the starting material ester can be completely reduced. The inorganic base is preferably used at a molar ratio of 1 to 5 with respect to the compound represented by the formula (1), so
10 that the product can be obtained in the form of inorganic salt.

Unlike the conventional methods, the method for preparing a salt according to the present invention uses an alcohol and an organic base in the first
15 step, instead of an aqueous solution of an inorganic base, and thereby makes it possible to selectively substitute only R_2 of the compound represented by the formula (1), thereby preventing the reaction intermediate substance from being hydrolyzed in the aqueous solution phase, and to solve the
20 problem that the reaction intermediate substance adheres to the reaction vessel during separation and purification of the substances in the aqueous solution phase. Thus, the yield is markedly increased.

Furthermore, the method for preparing a salt
25 according to the present invention reduces the conventional

three-step reaction process into a two-step reaction process by using an amine in the first step, so that the purification operation is simplified. The method of the present invention also allows the reduction reaction in the
5 second step to proceed by simply concentrating the solvent after the first step without any separation or purification processes. Thus, the method can provide the salt with high efficiency.

According to another embodiment of the present
10 invention, there is provided a salt prepared by the method for preparing a salt described above.

The method for preparing a salt of the present invention employs simple reaction steps, does not require purification processes, and is not accompanied by a
15 problem that reaction intermediate substances adhere to the reaction vessel during the purification processes, causing a decrease in yield.

Simple variations and modifications of the present invention can be easily carried out by those having ordinary
20 skill in the art, and these variations and modifications are all regarded to be included in the scope of the present invention.

Hereinafter, specific Examples of the present invention will be described. However, the Examples described below
25 are intended only for the purpose of specifically

illustrating or explaining the present invention, and are not intended to limit the present invention by any means. Furthermore, the subject matters that are not described herein can be sufficiently technically deduced by those skilled in the art, and therefore, detailed explanations thereon will be omitted.

EXAMPLES

[Example 1]

As shown in the reaction scheme 1 given below, 600 g (3.12 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 6 L of ether, and while the internal temperature was maintained at 18°C to 19°C, 133 ml (3.28 mol) of methanol (MeOH) was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 1.12 L (8.7 mol) of triethylamine (Net₃) was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B1) was confirmed by ¹H-NMR, and then the reaction solution was concentrated. The spectrum of ¹H-NMR obtained is presented in Fig. 1.

The crude reaction concentrate was dissolved in 6 L of tetrahydrofuran (THF) and 1.24 L of methanol, and in an ice bath, 362 g (9.57 mol) of sodium borohydride (NaBH₄) was slowly added dropwise to the solution. After the dropwise

addition, the ice bath was removed, and the temperature was raised to 60°C. The reaction mixture was stirred for about 4 hours at that temperature.

After the reaction was completed, the solvent was removed, the reaction concentrate was dissolved in 2 L (8 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to 4 was obtained. The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated.

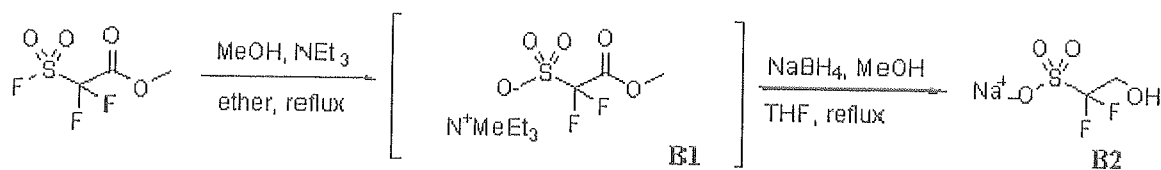
Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration. Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid (B2) obtained after filtration was dried in a vacuum, and the structure of the solid was confirmed by ^1H -NMR and ^{19}F -NMR. The results are presented in Fig. 2 and Fig. 3.

^1H -NMR (D_2O): (ppm) 4.16(t, 2H)

^{19}F -NMR (D_2O): (ppm) -115.3(t, 2F)

The solid was subjected to drying and filtration, and thus 495 g (yield 86.1%) of sodium 1,1-difluoro-2-hydroxyethanesulfonate (B2) was obtained.

[Reaction scheme 1]



[Example 2]

As shown in the reaction scheme 2 given below, 10 g (0.052 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 150 ml of ether, and while the internal temperature was maintained at 18°C to 19°C, 4.1 ml (0.055 mol) of n-propanol (n-PrOH) was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 18.1 ml (0.13 mol) of triethylamine (Net₃) was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B3) was confirmed by ¹H-NMR, and then the reaction solution was concentrated.

¹H-NMR (D₂O): (ppm) 3.59(s, 3H), 2.42(q, 6H), 2.34(q, 2H), 1.51(m, 2H), 1.05(t, 9H), 0.94(t, 3H)

The crude reaction concentrate was dissolved in 150 ml of tetrahydrofuran (THF) and 21.1 ml of methanol, and in an ice bath, 5.9 g (0.156 mol) of sodium borohydride (NaBH₄) was slowly added dropwise to the solution. After the dropwise addition, the ice bath was removed, and the temperature was raised to 60°C. The reaction mixture was stirred for about 4 hours at that temperature.

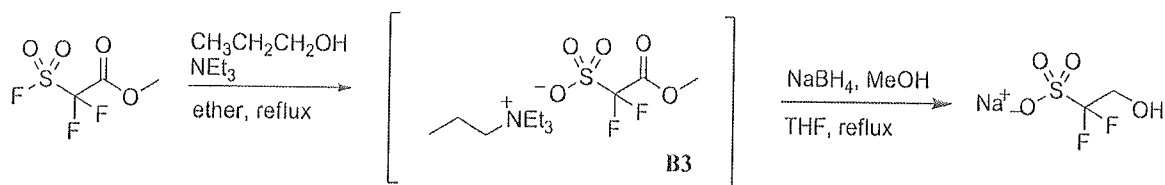
After the reaction was completed, the solvent was

removed, the reaction concentrate was dissolved in 50 ml (0.2 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to 4 was obtained. The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated.

Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration. Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum.

The solid was subjected to drying and filtration, and thus 7.5 g (yield 78%) of sodium 1,1-difluoro-2-hydroxyethanesulfonate was obtained.

[Reaction scheme 2]



[Example 3]

In the reaction of the first step, 10 g (0.052 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 150 ml of ether, and while the internal temperature was maintained at 18°C to 19°C, 4.2 ml (0.055 mol) of isopropanol

was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 18.1 ml (0.13 mol) of triethylamine (Net_3) was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B4) was confirmed by ^1H -NMR, and then the reaction solution was concentrated.

^1H -NMR (D_2O): (ppm) 3.58(s, 3H), 2.96(m, 1H), 2.42(q, 6H), 1.11(d, 6H), 0.97(t, 9H)

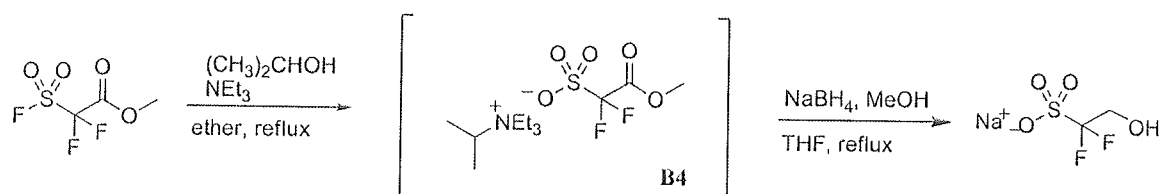
The crude reaction concentrate was dissolved in 150 ml of tetrahydrofuran (THF) and 21.1 ml of methanol, and in an ice bath, 5.9 g (0.156 mol) of sodium borohydride (NaBH_4) was slowly added dropwise to the solution. After the dropwise addition, the ice bath was removed, and the temperature was raised to 60°C . The reaction mixture was stirred for about 4 hours at that temperature.

After the reaction was completed, the solvent was removed, the reaction concentrate was dissolved in 50 ml (0.2 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to 4 was obtained. The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated.

Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration. Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum.

The solid was subjected to drying and filtration, and thus 7.2 g (yield 75%) of sodium 1,1-difluoro-2-hydroxyethanesulfonate was obtained.

[Reaction scheme 3]



[Example 4]

As shown in the reaction scheme 4 given below, 10 g (0.052 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 150 ml of ether, and while the internal temperature was maintained at 18°C to 19°C, 4.85 g (0.055 mol) of 4-hydroxy-2-butanone was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 18.1 ml (0.13 mol) of triethylamine (Net₃) was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B5) was confirmed by ¹H-NMR, and then the reaction solution was concentrated.

¹H-NMR (D₂O): (ppm) 3.67(s, 3H), 2.72(t, 2H), 2.58(t,

2H), 2.47(q, 6H), 2.11(s, 3H), 1.05(t, 9H)

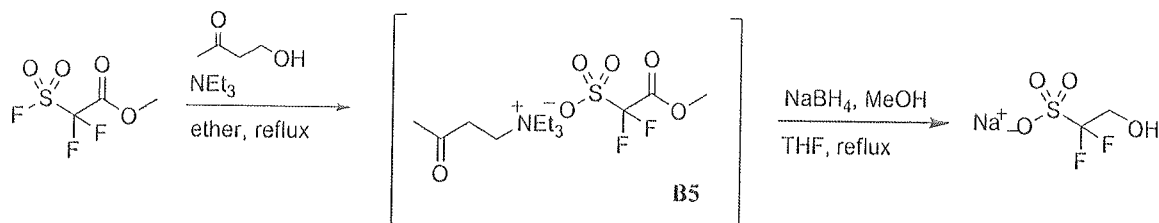
The crude reaction concentrate was dissolved in 150 ml of tetrahydrofuran (THF) and 21.1 ml of methanol, and in an ice bath, 5.9 g (0.156 mol) of sodium borohydride (NaBH_4)
5 was slowly added dropwise to the solution. After the dropwise addition, the ice bath was removed, and the temperature was raised to 60°C . The reaction mixture was stirred for about 4 hours at that temperature.

After the reaction was completed, the solvent was
10 removed, the reaction concentrate was dissolved in 50 ml (0.2 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to
15 4 was obtained. The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated.

Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration.
20 Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum.

The solid was subjected to drying and filtration, and thus 6.7 g (yield 70%) of sodium 1,1-difluoro-2-
25 hydroxyethanesulfonate was obtained.

[Reaction scheme 4]



[Example 5]

As shown in the reaction scheme 5 given below, 10 g
 5 (0.052 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 150 ml of ether, and while the internal temperature was maintained at 18°C to 19°C, 1.8 g (0.055 mol) of methanol was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 22.7 ml (0.13 mol)
 10 of N,N-diisopropylethylamine was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B6) was confirmed by ¹H-NMR, and then the reaction solution was concentrated.

15 ¹H-NMR (D₂O): (ppm) 3.71(s, 3H), 2.87(m, 1H), 2.45(q, 2H), 2.31(s, 3H), 1.15(d, 6H), 0.97(t, 3H)

The crude reaction concentrate was dissolved in 150 ml of tetrahydrofuran (THF) and 21.1 ml of methanol, and in an ice bath, 5.9 g (0.156 mol) of sodium borohydride (NaBH₄)
 20 was slowly added dropwise to the solution. After the dropwise addition, the ice bath was removed, and the temperature was raised to 60°C. The reaction mixture was

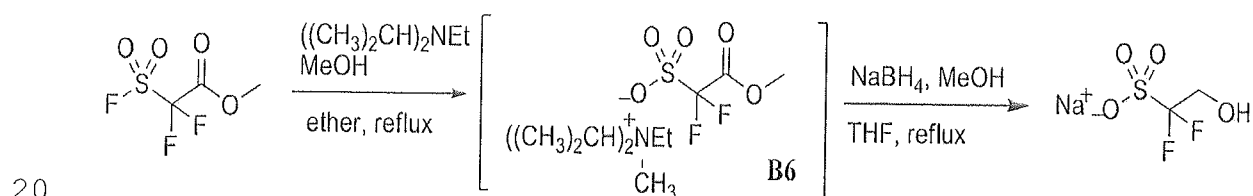
stirred for about 4 hours at that temperature.

After the reaction was completed, the solvent was removed, the reaction concentrate was dissolved in 50 ml (0.2 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to 4 was obtained. The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated.

Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration. Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum.

The solid was subjected to drying and filtration, and thus 7.7 g (yield 80%) of sodium 1,1-difluoro-2-hydroxyethanesulfonate was obtained.

[Reaction scheme 5]



[Example 6]

As shown in the reaction scheme 6 given below, 10 g

(0.052 mol) of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate was dissolved in 150 ml of ether, and while the internal temperature was maintained at 18°C to 19°C, 1.8 g (0.055 mol) of methanol was slowly added dropwise to the solution under stirring. After 30 minutes of stirring, 15.8 ml (0.13 mol) of 1-methylpiperidine was slowly added dropwise to the reaction mixture liquid, and the resulting mixture was heated to reflux for 12 hours. The presence of a reaction intermediate (B7) was confirmed by ¹H-NMR, and then the reaction solution was concentrated.

¹H-NMR (D₂O): (ppm) 3.58(s, 3H), 2.17(s, 6H), 1.81(t, 4H), 1.52-1.48(m, 6H)

The crude reaction concentrate was dissolved in 150 ml of tetrahydrofuran (THF) and 21.1 ml of methanol, and in an ice bath, 5.9 g (0.156 mol) of sodium borohydride (NaBH₄) was slowly added dropwise to the solution. After the dropwise addition, the ice bath was removed, and the temperature was raised to 60°C. The reaction mixture was stirred for about 4 hours at that temperature.

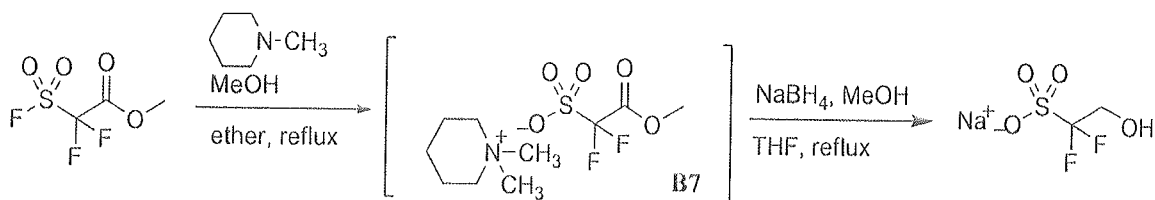
After the reaction was completed, the solvent was removed, the reaction concentrate was dissolved in 50 ml (0.2 mol) of a 4 N aqueous solution of sodium hydroxide (NaOH), and then the resulting solution was stirred for 4 hours. The solution was acidified with concentrated hydrochloric acid in an ice bath so that a pH value of 3 to

4 was obtained.

The reaction mixture liquid was washed with methylene chloride (MC), and the aqueous layer was concentrated. Methanol was introduced into the reaction concentrate, and any insoluble inorganic salt was removed by filtration. Methanol was concentrated, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum.

The solid was subjected to drying and filtration, and thus 7.2 g (yield 75%) of sodium 1,1-difluoro-2-hydroxyethanesulfonate was obtained.

[Reaction scheme 6]



[Comparative Example]

As shown in the reaction scheme 7 given below, as a first step reaction, 750 g of water was introduced to 300 g of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate, and while the mixture was stirred, a 30% aqueous solution of sodium hydroxide was slowly added dropwise to the mixture. Subsequently, the mixture was heated to reflux for 3 hours under stirring. After the reaction mixture was cooled, the reaction mixture liquid was neutralized using concentrated

hydrochloric acid, and the reaction mixture liquid was concentrated to obtain 416 g of sodium carboxydifluoromethanesulfonate (containing inorganic salts, yield: 75%, purity: 60%).

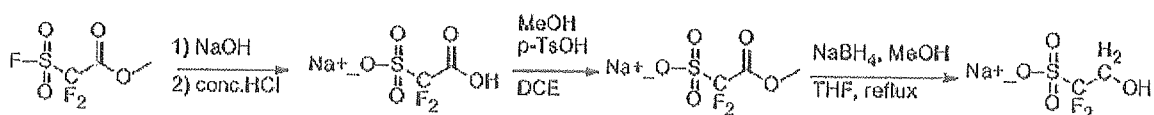
5 As a second step reaction, 322 g of sodium carboxydifluoromethanesulfonate (purity: 60%) and 104 g of methanol (MeOH) were dissolved in 1.5 L of dichloroethane (DCE), and 186 g of p-toluenesulfonic acid (p-TsOH) was added to the solution. Then, the reaction mixture was
10 heated to reflux for 5 hours. The mixture was concentrated to remove dichloroethane, and then 1.5 L of acetonitrile was added thereto. The resulting mixture was stirred. The stirred mixture was filtered and concentrated, and thus sodium 1,1-difluoro-2-methoxy-2-oxoethanesulfonate (38 g,
15 yield: 20%).

As a third step reaction, 83 g of 1,1-difluoro-2-methoxy-2-oxoethanesulfonate was dissolved in 160 ml of methanol and 1.2 L of tetrahydrofuran (THF) in an ice bath, and 44 g of sodium borohydride (NaBH_4) was slowly added
20 dropwise thereto. After the dropwise addition, the ice bath was removed, the temperature was raised to 60°C, and the mixture was stirred for about 4 hours. After the reaction, the reaction mixture liquid was quenched with distilled water, and then the solvent was removed. The crude reaction
25 mixture was dissolved again in distilled water, and the

solution was acidified with concentrated hydrochloric acid so that a pH value of 5 to 6 was obtained. The reaction mixture was concentrated, and then methanol was introduced thereto. The resulting slurry was filtered to remove
 5 inorganic salts, and the filtrate was washed two times with hexane. The methanol layer was concentrated again, and then crystallization was carried out using diethyl ether. A white solid obtained after filtration was dried in a vacuum, and thus 68.5 g (yield 95%) of sodium 1,1-difluoro-2-
 10 hydroxyethanesulfonate was obtained.

In the Comparative Example, the overall yield of the reaction was 14.2%.

[Reaction scheme 7]



15 The yields of sodium 1,1-difluoro-2-hydroxyethanesulfonate produced in the Examples 1 to 6 and the Comparative Example are presented in the following Table 1.

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example
No. of reaction steps	Two-step	Two-step	Two-step	Two-step	Two-step	Two-step	Three-step
Overall yield (%)	86.1	78	75	70	80	75	14.2

It can be seen from the above results that in the case of the Comparative Example, the yield markedly drops in the second reaction step. This seems to be a problem occurring because the reaction in the Comparative Example was carried
5 out using an aqueous solution of sodium hydroxide, and therefore, sodium carboxydifluoromethanesulfonate adheres to the reaction vessel during the purification process after the first reaction step.

On the contrary, Examples 1 to 6 are all achieved not
10 by a three-step reaction but by a two-step reaction, and as a result of carrying out the reaction using an alcohol and an amine, a significantly high yield of 70 to 86.1% is obtained.

The foregoing description of preferable exemplary
15 embodiments of the present invention has been provided in detail, but the scope of rights of the present invention is not intended to be limited to these. Many variations and modifications of the present invention that may be made by those skilled in the art based on the basic concept of the
20 invention as defined by the following claims, also belong to the scope of rights of the present invention.

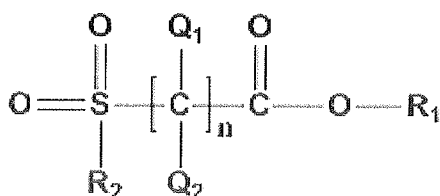
WHAT IS CLAIMED IS:

1. Method for preparing a salt, comprising:

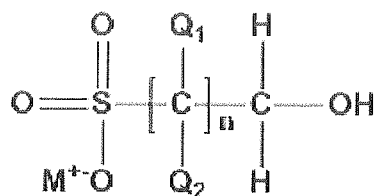
5 reacting a compound represented by the following formula (1) with an alcohol and an amine to obtain an ammonium salt; and

reacting the ammonium salt with a reducing agent and an inorganic base to obtain a compound represented by the following formula (2):

[Formula 1]



[Formula 2]



15 wherein in the formulas (1) and (2),

R₁ and R₂ each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a

heterocycloalkyl group, an aryl group and a heteroaryl group;

Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom,
5 and a perfluoroalkyl group;

M represents any one selected from the group consisting of lithium (Li), sodium (Na), potassium (K) and silver (Ag); and

n is an integer from 1 to 10.

10

2. Method for preparing a salt according to claim 1, wherein the amine is any one selected from the group consisting of a primary amine, a secondary amine, a tertiary amine and combinations thereof.

15

3. Method for preparing a salt according to claim 1, wherein the alcohol is a compound represented by the following formula (3), and the amine is a compound represented by the following formula (4):

20 [Formula 3]

R₃OH

[Formula 4]

NR₄R₅R₆

wherein in the formulas (3) and (4),

25 R₃ represents any one selected from the group consisting

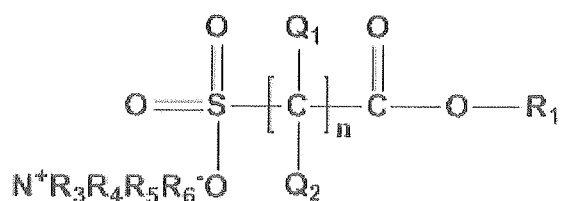
of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an alkoxy group, an aryl group and a heteroaryl group;

R₄ to R₆ each independently represent an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group; and

when R₅ and R₆ are alkyl groups, they may be linked together to form a hydrocarbon ring.

4. Method for preparing a salt of claim 3, wherein the ammonium salt is a compound represented by the following formula (5):

[Formula 5]



wherein R₁ represents any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, and a perfluoroalkyl group;

R₃ represents any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an alkoxy group, an aryl group and a heteroaryl group;

5 R₄ to R₆ each independently represent any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

when R₅ and R₆ are alkyl groups, they may be linked
10 together to form a hydrocarbon ring; and

n is an integer from 1 to 10.

5. Method for preparing a salt according to claim 1, wherein the alcohol is any one selected from the group
15 consisting of methanol, ethanol, propanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, oxobutyl alcohol, undecyl alcohol, hydroxydecyl alcohol, heptyl alcohol, 2-methyl-1-pentyl alcohol, allyl alcohol, ethoxycarbonylmethyl alcohol, methoxyethyl alcohol, 1-
20 methoxy-2-propyl alcohol, benzyl alcohol, phenethyl alcohol, cyclohexyl alcohol, menthyl alcohol, tetrahydrofurfuryl alcohol, tetrahydropyranyl alcohol, cyanobutyl alcohol, 4-hydroxy-2-butanone and combinations thereof.

25 6. Method for preparing a salt according

to claim 1, wherein the reducing agent is any one selected from the group consisting of $(\text{CH}_2)_4\text{O}$ (tetrahydrofuran, THF), NaBH_4 , LiAlH_4 , $\text{BH}_3\text{-THF}$, $\text{NaBH}_4\text{-AlCl}_3$, $\text{NaBH}_4\text{-LiCl}$, LiAl(OMe)_3 and combinations thereof.

5

7. Method for preparing a salt according to claim 1, wherein the inorganic base is a salt formed from any one cation selected from the group consisting of alkali metals and alkaline earth metals, and any one anion selected from a
10 sulfate ion, a nitrate ion, a chloride ion, a bromide ion, an iodide ion and a thiocyanate ion.