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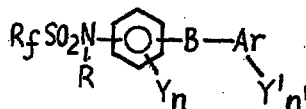
(54) FLUOROALKYLSULFONAMIDOARYL COMPOUNDS

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America of 3M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to aryl-substituted fluoroalkylsulfonanilides in which the aryl group comprises phenyl or naphthyl linked by oxygen, sulfur, sulfinyl or sulfonyl, and to salts thereof. The rings and the fluoroalkylsulfonamido nitrogen are optionally substituted. The compounds are active herbicides and some are anti-inflammatory agents. Methods for the use of the compounds are also included.

Although diphenylethers, diphenylthioethers, diphenylsulfoxides and diphenylsulfones which are substituted by chloroaryl-, chloroalkyl-, chloroaralkyl- and chlorocycloalkylsulfonamido groups have been alluded to (see British patent 854,956), there has been no suggestion of herbicidal activity of such compounds.

According to the present invention, there is provided a class of compounds of the formula



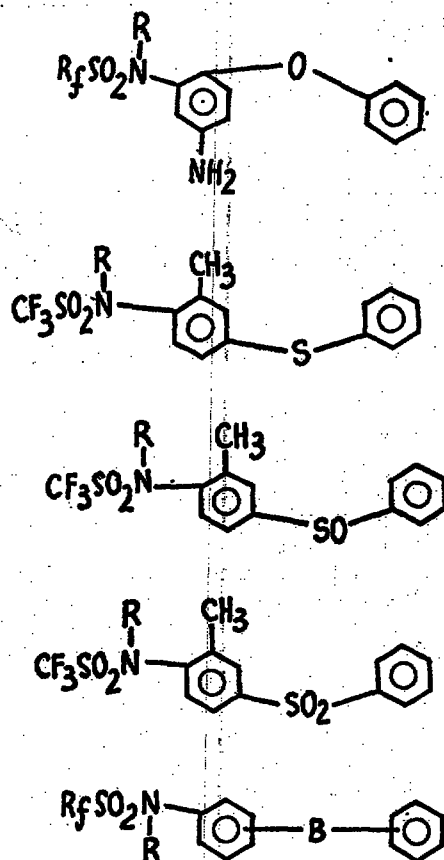
wherein R_f is a lower fluoroalkyl radical having at least two fluorine atoms bonded to the alpha carbon atom, R is hydrogen, a cation, cyano, alkyl, alkylsulfonyl, or

—C(=O)—A—R' , where R' is alkyl and A is oxygen or a carbon-carbon bond, B is oxygen, sulfur, sulfinyl or sulfonyl, Ar is phenyl or naphthyl, the or each Y and the or each Y' is selected independently from halogen, alkyl, alkoxy, nitro, amino, alkanamido, haloalkyl, hydroxy, dialkylamino, carbalkoxamino, alkylthio, alkylsulfonyl, alkanoyl, dialkylsulfamoyl and alkylsulfinyl and n and n' are independently zero, one or two provided that any individual aliphatic groups appearing in the compounds of Formula I (i.e. in R_f , R, R' , Y and Y') contain from one to four carbon atoms. When n is zero, the phenyl ring adjacent to the fluoroalkylsulfonamido group is unsubstituted except for that group and the group connected thereto through B. Similarly, when n' is zero, Ar is unsubstituted except for the group shown in the formula and attached thereto through B.

Compounds of the invention wherein R is hydrogen or a cation are presently preferred. Preferably, also, the individual aliphatic groups in R_f , R, R' , Y and Y' contain one carbon atom. Preferred for anti-inflammatory purposes are the compounds in which Y and Y' are nitro or amino.

R_f may be either a straight or branched chain fluoroalkyl radical and preferably contains one or two carbon atoms. Most preferably R_f is trifluoromethyl, since the herbicidal activity of the compounds of the invention is generally greater when R_f is perfluorinated and when R_f has one carbon atom.

Preferred groups of compounds according to the invention include those of the formula:



for example 5-amino-2-phenoxytrifluoromethanesulfonanilide, 2-methyl-4-phenylthio-trifluoromethanesulfonanilide, 2-nitro-4-phenylthiotrifluoromethanesulfonanilide, 2-methyl-4-phenylsulfinyltrifluoromethanesulfonanilide and 2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide.

The compounds of the invention are acidic in nature when R is hydrogen. Consequently, they form salts, i.e. compounds of Formula I wherein R is a cation. The pharmaceutically or horticulturally acceptable salts are generally metal, ammonium and organic amine salts and can be prepared by treating the acid form (compounds of Formula I in which R is hydrogen) with a stoichiometrically equivalent amount of an appropriate base under mild conditions. Among the metal salts of the invention are alkali metal (e.g. lithium, sodium and potassium), alkaline earth metal (e.g. barium, calcium and magnesium) and heavy metal (e.g. zinc and iron) salts as well as other metal salts such as aluminum. Appropriate bases for use in preparing the metal salts include metal oxides, hydroxides, carbonates, bicarbonates and alkoxides. Some salts are also prepared by cation exchange reactions (by reacting a salt of the invention with an organic or inorganic salt in a cation exchange reaction). The organic amine salts include the salts of aliphatic (e.g. alkyl), aromatic and heterocyclic amines, as well as those having a mixture of these types of structures. The amines useful in preparing the salts of the invention can be primary, secondary or tertiary and preferably contain not more than 20 carbon atoms. Such amines include, for example, morpholine, methyl cyclohexylamine, glucosamine, etc. These and the ammonium salts can be prepared by reacting the acid form with the appropriate organic base or ammonium hydroxide. The pharmaceutically acceptable salts are generally the alkali metal, alkaline earth, ammonium and amine salts. Any of the salts of the types set out above are agriculturally acceptable, the one chosen depending

upon the particular use and upon the economics of the situation.

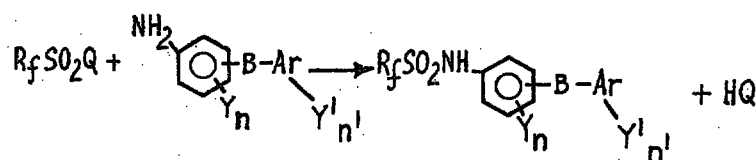
The salts of the invention are frequently formed by reacting the precursors in aqueous solution. This solution can be evaporated to obtain the salt of the compound, usually as a dry powder. In some cases, it may be more convenient to use a non-aqueous solvent such as alcohols, acetone, etc. The resulting solution is then treated to remove the solvent, for example, by evaporation under reduced pressure. Since many of the salts are water soluble, they are often used in the form of aqueous solutions. Also, they can be used in making pharmaceutical preparations in the form of capsules for oral administration.

The compounds of this invention wherein R is hydrogen (the acid form) are preparable by two different methods from precursors (i.e. compounds not falling within the scope of Formula I) and, in addition, certain of the compounds of Formula I are preparable from other compounds of Formula I.

Preparation of the Compounds of Formula I from Precursors

Method A

This is the most general process and can be described as follows



II

where Q is a halogen or the OSO₂R_f grouping and R_f, B, Ar, Y, Y', n and n' are as previously defined. The reaction is usually run in the presence of a suitable acid acceptor, which may be an organic or inorganic base. When Q is halogen it is preferably fluorine.

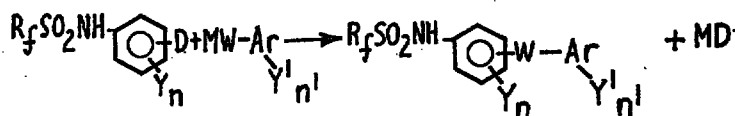
A solution of the appropriate primary arylamine of Formula II and at least an equimolar quantity of a suitable acid acceptor (such as dimethylaniline or triethylamine) in an inert organic solvent is prepared. Among the suitable solvents are diglyme, benzene, dichloromethane and chloroform. An equimolar quantity of the appropriate fluoroalkanesulfonic anhydride or halide is added to the solution. The addition is advantageously carried out at -15° to 150°C., but this may be raised or lowered if desired. In cases where the amine is of lower reactivity, it is advantageous to allow the reaction mixture to remain at reflux temperature for a few hours following addition.

After completion of the reaction, the product is isolated by conventional methods. For example, the reaction mixture can be extracted with excess aqueous sodium hydroxide. The aqueous extract is then washed with organic solvents and treated with charcoal to remove impurities. Subsequent acidification of the aqueous extract with mineral acid then affords the product as an oil or solid which is distilled, sublimed, chromatographed or recrystallized as required to give pure product. When water-soluble solvents are used, the reaction mixture can be poured directly into aqueous mineral acids. The product is then isolated by conventional extraction techniques and purified as above.

The reaction may also be run in a closed reactor, and when this is done solvent is not usually necessary, and Q is usually fluorine, although an acid acceptor, generally triethylamine, is necessary. The temperatures utilized depend on the reactivity of the reactants, but may be between 0 and 200°C., and are generally 50 to 150°C.

Method B

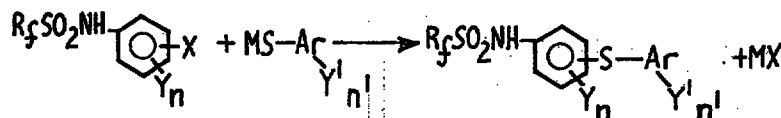
Some of the compounds of the invention can also be prepared by the nucleophilic displacement reaction of a metal salt of an aromatic compound with a halogen derivative or diazonium salt as follows:



wherein D is halogen (chlorine, bromine or iodine) or a diazonium group (e.g.

$-\text{N}=\text{N}^{\oplus}\text{Cl}^{\ominus}$), M is alkali metal and W is $-\text{O}-$ or $-\text{S}-$, provided that when D is halogen, M can also be copper and provided further that where D is a diazonium group, W cannot be oxygen. The following three specific methods are included within B.

Method B 1.

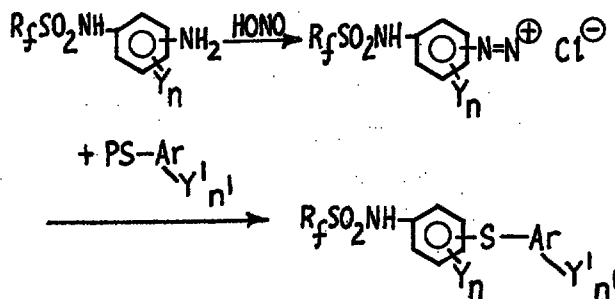


where Y, Y', n, n', M and R_f are as previously defined and X is halogen (chlorine, bromine or iodine). Solvents used in the reaction are pyridine-quinoline mixtures or dimethylformamide. Temperatures of 125° to 200°C. are generally necessary to obtain reaction. The reaction is generally run in the presence of a base, which serves as an acid acceptor. Suitable bases may be organic, for example pyridine, or inorganic, for example sodium bicarbonate. The reaction time is usually 6 hours to 3 days, and extended reaction periods are frequently necessary to obtain appreciable results.

M must be copper unless Y is an electron-withdrawing group, then it may be an alkali metal. When M is copper the solvent is preferably pyridine-quinoline. When M is an alkali metal, dimethylformamide is a suitable solvent.

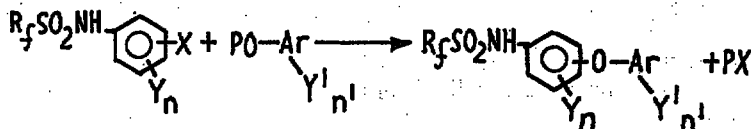
The thiophenols, thionaphthols and salts are known in the chemical literature. The substituted fluoroalkylsulfonamidobenzene derivatives are known in the chemical literature and are described in South African patent 68/4125, or can be prepared by the methods described in said patent from known starting materials.

Method B 2.



where R_f, Ar, Y, Y', n, and n' are as defined above and P is an alkali metal. This reaction is carried out by adding the cold diazonium salt solution to the refluxing aqueous solution of the alkali metal thiophenoxide salt or the corresponding naphthalene derivative.

Method B 3.

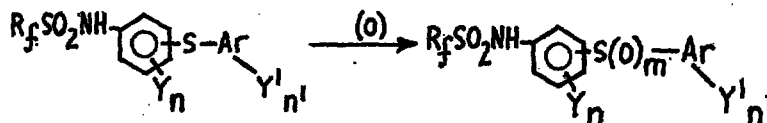


where Y, Y', n, n', R_f, Ar, P and X are as previously defined. Solvents used in the reaction are pyridine, quinoline, dimethylformamide and the like. When X is chlorine Y must be an activating group such as nitro. Cuprous chloride is a suitable cuprous catalyst for the reaction. The alkali metal salts may be preformed or formed *in situ*. Temperatures of 0 to 200°C. may be used, depending upon the reactivity of the substrates. Extended reaction periods are sometimes necessary.

Preparation of Compounds of Formula I from Other Compounds of Formula I

Method C

This relates to preparation of the diarylsulfoxides and diarylsulfones by oxidation of the diarylthioethers as follows



where R_f , Ar , Y , Y' , n and n' are as previously defined and m is one or two. Suitable oxidizing methods are well known to the art, for example hydrogen peroxide, peracids such as peracetic and perbenzoic acid, sodium metaperiodate and the like.

Method D

This includes the various ways in which Y and Y' are changed in the compounds of Formula I. For example, compounds wherein Y or Y' is amino are prepared by reduction of nitro compounds, compounds wherein Y or Y' is alkanamido are prepared by acylation of amino compounds, compounds of Formula I wherein R is hydrogen can be nitrated or halogenated on the phenyl rings. When Y or Y' is alkylthio it is readily oxidized to alkylsulfinyl or alkylsulfonyl. Compounds wherein Y or Y' is hydroxy and R is hydrogen are preferably prepared by simple hydrogen iodide cleavage of the corresponding compound wherein Y or Y' is alkoxy. When Y or Y' is amino, it can be converted to dialkylamino by known methods.

Method E

This includes the various ways in which R is changed in compounds of Formula I. The preparation of the salts (wherein R is a cation) from the acid form compounds has already been discussed. To prepare the compounds of the invention wherein R is lower alkyl compounds of Formula I wherein R is a metal ion, for example sodium or potassium, are reacted with a stoichiometric amount of alkyl bromide or iodide or a dialkyl sulfate in a non-reactive solvent such as acetone.

Compounds of the invention wherein R is cyano are prepared by reacting the corresponding compounds of the invention wherein R is a cation such as sodium or potassium with cyanogen chloride or bromide in a non-reactive solvent.

Compounds of the invention wherein R is alkylsulfonyl are prepared by reacting the corresponding compounds of the invention wherein R is a cation such as sodium or potassium with an alkylsulfonyl chloride.

Compounds of the invention wherein R is a $-\overset{\overset{O}{\parallel}}{C}-A-R'$ radical are prepared by reacting the corresponding compounds wherein R is a cation with an acylating agent of the formula

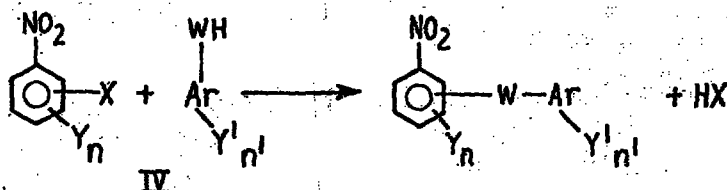


wherein A and R' are as defined hereinabove and E is halogen, preferably fluorine, chlorine or bromine, or the residue of an anhydride, i.e. an acyloxy group.

Precursors

Suitable fluoroalkanesulfonyl anhydrides and halides (for example chlorides and fluorides) for use in preparing compounds of Formula I are known to the art. The primary arylamines of Formula II are also either known to the art, or may be made by methods well known to the art, generally by the reduction of the corresponding nitro compound. Conventional reduction techniques, both chemical and catalytic, well known to the art are used, such as iron in acetic acid, sodium sulfide, and most commonly Raney nickel and hydrogen gas. The nitro compound precursors of the compounds of Formula II are also known to the art, or may be prepared by well known methods, as described (Methods (1)-(5)) and exemplified hereinafter.

Method (1)



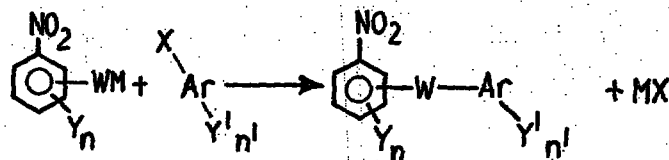
where Ar, Y, Y', n and n' are as previously defined, W is oxygen or sulfur and X is chlorine, bromine or iodine. Although the reaction may be run in the presence of a base which acts as an accelerator and acid acceptor, it is preferably carried out by prereacting the compound of Formula IV with base to form a salt, and salts of inorganic bases are preferred. It is well known that such salts are readily prepared, and they may be prepared *in situ*, or isolated. Most preferred are salts of alkali metals, such as sodium and potassium, or cuprous salts. When W is oxygen, copper salts are not isolated. When alkali metal salts are used, dimethylformamide and pyridine are preferred solvents. When Y is an electron-donating substituent such as alkyl or alkoxy in the 2 or 4 positions relative to the nitro group and W is oxygen, pyridine is the preferred solvent, and a trace of cuprous chloride is used as catalyst.

Cuprous salts are particularly useful for the preparation of 3-phenylthionitrobenzene derivatives, and in this case X is generally not chlorine. When cuprous salts are used a preferred solvent mixture is quinoline and pyridine.

Cuprous salts or cuprous chloride catalyst and pyridine as solvent are preferred in order to prepare 3-phenoxy nitrobenzenes. It is preferred that X is bromine or iodine, since higher yields are obtained, although when X is chlorine some product is usually isolable.

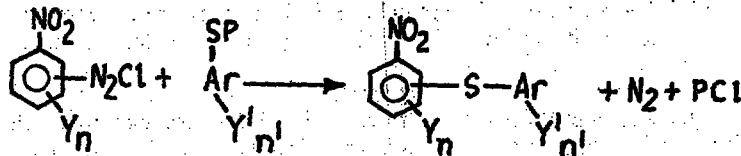
When Y is an electron-donating substituent or when a compound wherein W is oriented meta to the nitro group is the desired product it is preferred that W is oxygen, pyridine is the solvent, cuprous chloride is used as a catalyst and a sodium salt of the compound of Formula IV is preformed.

Method (2)



where Ar, Y, Y', W, X, M, n and n' are as previously defined, provided that M is preferably copper in the cuprous form. When Y is an electron-withdrawing group M may be an alkali metal, but in all cases it is preferred that M is copper and X is bromine or iodine. A cuprous catalyst can also be used.

Method (3)



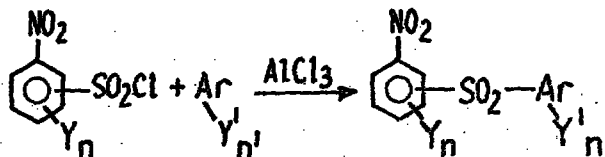
where Ar, Y, Y', n and n' are as previously defined and P is an alkali metal.

Method (4)

The compounds of Formula II wherein B is a sulfinyl or sulfonyl group can be prepared by the oxidation of the nitro compounds which are precursors of compounds of Formula II wherein B (or W) is sulfur. This oxidation is done using conventional methods such as hydrogen peroxide or sodium metaperiodate.

Method (5)

The nitro compounds which are precursors of compounds of Formula II wherein B is a sulfonyl group can be prepared by the Friedel-Crafts reaction as follows:



The starting materials necessary for use in Methods (1), (2), (3), (4) and (5) are known to the art and are in the general chemical literature.

A wide variety of acylating agents of Formula III can be used in preparing the compounds of the invention, including acyl halides or anhydrides or haloformates. These compounds are either available directly, or in the case of certain chloroformates are easily prepared from phosgene and the appropriate alcohol.

As noted previously, the compounds of the invention are active herbicides and some are also anti-inflammatory agents. Further, some are analgesic and anti-pyretic agents and some have been found to possess anti-microbial activity. Compounds of the invention wherein B is oxygen are generally more active as anti-inflammatory and analgesic agents, most particularly those in which R₁ contains one carbon atom, R is hydrogen or a pharmaceutically acceptable cation and Ar is phenyl.

Some compounds of the invention are acidic and are also useful as catalysts or initiators for certain polymerizations, the perfluoroalkyl derivatives being particularly useful in this regard. When so used, the compounds are mixed with the monomer or prepolymer. Suitable monomers include epoxide and vinyl ether monomers. The rate of reaction and the degree of polymerization varies depending upon the temperature at which the polymerization is carried out and the reactivity of the monomer, and heating of the polymerization reaction is generally utilized to obtain a faster polymerization rate.

The herbicidal activity of representative compounds of Formula I has been determined using screening tests against experimental plantings. Both pre- and post-emergence activity are determined in a direct screen against selected weed species. The following weed mixtures are used for the tests.

Grasses:

Giant foxtail (*Setaria faberii*)
 Barnyard grass (*Echinochloa crusgalli*)
 Crabgrass (*Digitaria ischaemum*)
 Quackgrass (*Agropyron repens*)

Broadleaves:

Pigweed (*Amaranthus retroflexus*)
 Purslane (*Portulaca oleracea*)
 Wild Mustard (*Brassica kaber*)
 Wild morning glory (*Convolvulus arvensis*)

The test chemicals are dissolved in a small amount of acetone or other suitable solvent and then diluted with water to give a concentration of 2000 ppm. From this concentration aliquots are diluted to give a final concentration of 500 ppm. Eighty ml. of this solution are added to a 6-inch pot containing the weed seeds to give a concentration equivalent to 20 lb./acre. All subsequent waterings are made from the bottom. Two pots are used per treatment. Data are taken two to three weeks after treatment and recorded as percent pre-emergence kill for each species compared to the untreated controls. Some screening is done at 40 lb./acre.

To assess post-emergence activity, the same weed mixtures are allowed to grow from 2 to 3 weeks until the grasses are approximately 1 to 3 inches and the broad-leaves 1-1/2 inches tall. They are sprayed for approximately 10 seconds or until good wetting of the leaf surfaces occurs with a 2000 ppm solution as described above.

Data are taken two to three weeks after treatment and recorded as percent kill for each species compared to the untreated controls.

The compounds of this invention are broadly active as herbicides. The mechanism(s) by which this herbicidal activity is effected is not presently known.

However, many of the compounds of this invention also show various types of plant growth modifying activity. Plant growth modification as defined herein consists of all deviations from natural development, for example defoliation, stimulation, stunting, retardation, desiccation, tillering, dwarfing and regulation. This plant growth modifying activity is generally observed as the compounds of the invention begin to interfere with certain processes within the plant. If these processes are essential, the plant will die if treated with a sufficient dose of the compound. However, the type of growth modifying activity observed varies among types of plants. It has been found that with certain compounds of the invention, herbicidal activity can be separated from certain desirable growth modifying activities by controlling the rate of application. Of particular interest is the ability of some compounds of the invention to give tobacco sucker control. This phenomenon is known to the art to be desirable and useful, since the control of tobacco suckers increases the useful yield of the tobacco plant. This desirable and useful activity is present in a particularly high degree in 2-methyl-4-phenylthiotrifluoromethanesulfonanilide and 2-nitro-4-phenylthiotrifluoromethanesulfonanilide.

Some of the compounds of the invention have been found to be particularly effective in controlling nutsedge (for example *Cyperus esculentus* and *Cyperus rotundus*) species. Nutsedge is considered one of the major weed pests of the world. This weed is resistant to most herbicides, and has become an increasingly severe problem. It is a particularly severe problem when other weed species are controlled by herbicides and nutsedge becomes the dominant weed. It was unexpected to find outstanding control of nutsedge in the compounds of the invention. Compounds of the invention wherein

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—C—A—R'

B is sulfur, sulfinyl or sulfonyl, R_n is CF₃, R is hydrogen, a cation or —C—A—R', n and n' are zero or one, Y and Y' are lower alkyl or halogen and the fluoroalkyl-sulfonamido group is oriented meta or para to B are presently preferred due to nutsedge activity.

Presently preferred herbicidal compounds of this invention are

3-Phenylsulfinyltrifluoromethanesulfonanilide,
2-Methyl-5-phenylsulfinyltrifluoromethanesulfonanilide,
2-Methoxy-4-phenylsulfinyltrifluoromethanesulfonanilide,
3-(4'-Fluorophenylthio)trifluoromethanesulfonanilide,
2-Phenylthiotrifluoromethanesulfonanilide,
3-Phenylthiotrifluoromethanesulfonanilide,
4-Phenylthiotrifluoromethanesulfonanilide,
4-Phenoxytrifluoromethanesulfonanilide,
2-Methyl-4-phenylsulfinyltrifluoromethanesulfonanilide,
5-Chloro-2-phenoxytrifluoromethanesulfonanilide,
4-(4-Acetamidophenylthio)trifluoromethanesulfonanilide,
2-Methyl-4-phenylthiotrifluoromethanesulfonanilide,
2-Methyl-4-phenylsulfonyltrifluoromethanesulfonanilide,
4-Phenylthio-2-nitrotrifluoromethanesulfonanilide,
4-Phenylsulfonyltrifluoromethanesulfonanilide,
2-Methyl-3-phenylthiotrifluoromethanesulfonanilide,
4-Phenylsulfinyltrifluoromethanesulfonanilide,
2-Methyl-5-phenylthiotrifluoromethanesulfonanilide,
3-Phenylsulfonyltrifluoromethanesulfonanilide, N - Carbethoxy - 2 - methyl - 4 - phenylsulfonyltrifluoromethanesulfonanilide,
N-Carbethoxy-2-methyl-4-phenylthiotrifluoromethanesulfonanilide.

For application to plants, the compounds can be finely divided and suspended in any of the usual aqueous media. In addition, spreading agents, wetting agents, sticking agents or other adjuvants can be added as desired. Dry powders, as such or diluted with inert materials such as diatomaceous earth, can likewise be used as dusts for this purpose. The preparations are coated on the plants or the ground is covered with pre-emergence control is desired. Application is made with the usual sprayers, dust guns and the like. Application rates are at 0.5 to 20 lbs./acre in general, but may be increased or reduced according to individual circumstances of use.

The anti-inflammatory activity can be conveniently demonstrated using assays designed to test the ability of these compounds to antagonize the local edema characteristic of the inflammatory response (rat foot edema test) and to inhibit the onset of the erythematous manifestation of inflammation (guinea pig erythema test). Leading references to the rat foot edema test are:

1. Adamkiiewicz et al, *Canad. J. Biochem. Physio.* 33:332, 1955;
2. Selye, *Brit. Med. J.* 2:1129, 1949 and
3. Winter, *Proc. Soc. Exper. Biol. Med.* 111:554, 1962.

Leading references to the guinea pig erythema test are:

1. Wilhelmi, *Schweiz. Med. Wschr.* 79:557, 1949 and
2. Winder et al, *Arch. Int. Pharmacodyn* 116:261, 1958.

Analgesic activity has been observed in standard test methods such as the Randall-Selitto and phenylquinone writhing tests. Anti-inflammatory activity may also be detected by assays known to the art such as the cotton pellet granuloma and adjuvant arthritis tests.

The compounds are administered orally, for example as four percent acacia suspensions, but may also be administered parenterally. Amounts are generally about 1 to 500 mg./kg. of body weight of the mammal to be treated.

The presently preferred compounds of the invention with respect to anti-inflammatory activity include:

2-Phenylthiotrifluoromethanesulfonanilide,
 5-Amino-2-phenoxytrifluoromethanesulfonanilide,
 3-Phenylthiotrifluoromethanesulfonanilide,
 5-Hydroxy-2-phenoxytrifluoromethanesulfonanilide,
 2-Phenoxytrifluoromethanesulfonanilide,
 5-Chloro-2-phenoxytrifluoromethanesulfonanilide,
 5-Methyl-2-phenoxytrifluoromethanesulfonanilide,
 4-Amino-2-phenoxytrifluoromethanesulfonanilide,
 2-(4'-Chlorophenoxy)trifluoromethanesulfonanilide,
 4-Nitro-2-phenoxytrifluoromethanesulfonanilide,
 3-Phenoxytrifluoromethanesulfonanilide,
 5-Amino-2-phenylthiotrifluoromethanesulfonanilide,
 3-(4'-Methoxyphenoxy)trifluoromethanesulfonanilide,
 4-Nitro-2-phenylthiotrifluoromethanesulfonanilide,
 2-(4-Chlorophenoxy)-4-nitrotrifluoromethanesulfonanilide,
 5-Methyl-4-nitro-2-phenoxytrifluoromethanesulfonanilide,
 4-Nitro-2-phenoxydifluoromethanesulfonanilide and the pharmaceutically acceptable salts of these compounds.

The anti-microbial activity of the compounds is evaluated using a variation of the original agar-plate diffusion method of Vincent and Vincent (e.g. see Vincent, J. G., and Vincent, Helen W., *Proc. Soc. Exptl. Biol. Med.* 55:162—164, 1944, and Davis, B. D., and Mingioli, E. S., *J. Bac.* 66:129—136, 1953).

The following examples are given for the purpose of further illustrating the procedures of the present invention, but are not intended, in any way, to be limiting on the scope thereof. Thus, while the great majority of the examples relate to trifluoromethanesulfonamides, other fluoroalkyl groups can be substituted in place thereof. Also, to avoid unduly multiplying the examples which have been selected to illustrate the invention, the examples will relate for the most part to compounds in which R is hydrogen. It is, however, understood that the corresponding compounds in which R is a cation are also easily prepared and are likewise contemplated. Such compounds (in which R is a cation) are also useful as herbicides.

All melting points in the examples are uncorrected. The boiling points and melting points are given in degrees Centigrade and the pressures in millimeters of mercury.

Example 1 relates to the preparation of compounds of Formula I by Method A.

Example 1

A mixture of 3-thiophenoxyaniline (20.0 g., 0.099 mole), triethylamine (15.4 ml., 0.11 mole) and chloroform (125 ml.) are treated with trifluoromethanesulfonic anhydride (16.8 ml., 0.10 mole) during a ninety minute period under a nitrogen atmosphere. After stirring ninety minutes ten percent hydrochloric acid (150 ml.) is added and the chloroform is removed *in vacuo*. The residue is taken up in ten percent sodium hydroxide (150 ml.), the solution is extracted with diethyl ether and the aqueous layer is acidified. An oil forms, and extraction of the aqueous layer with diethyl ether is followed by drying of the ether layer over magnesium sulfate. Fractional distillation yields 3-phenylthiotrifluoromethanesulfonanilide, b.p. 174°C/0.15 mm., m.p. 56.5—58°C.

Analysis:

Calculated for $C_{13}H_{10}F_3NO_2S_2$: C, 46.9; H, 3.0

Found: C, 46.9; H, 3.0

The following compounds are also prepared using general Method A:

- | | | |
|----|---|----|
| 5 | 3-(2,3-dimethylphenoxy)trifluoromethanesulfonanilide, m.p. 62—63°C. | 5 |
| | 3-(4-chlorophenoxy)trifluoromethanesulfonanilide, b.p. 156°C./0.19 mm. | |
| | 3-(3-chlorophenoxy)trifluoromethanesulfonanilide, b.p. 164°C./0.08 mm. | |
| | 3-(2-chlorophenoxy)trifluoromethanesulfonanilide, b.p. 156°C./0.06 mm. | |
| 10 | 3-(4-methoxyphenoxy)trifluoromethanesulfonanilide, b.p. 153°C./0.35 mm. | 10 |
| | 3-(3-trifluoromethylphenoxy)trifluoromethanesulfonanilide, b.p. 158°C./0.23 mm. | |
| | 3-(4-methylphenylthio)trifluoromethanesulfonanilide, b.p. 147°C./0.03 mm. | |
| | 3-(4-methoxyphenylthio)trifluoromethanesulfonanilide, b.p. 197—201°C./0.22 mm. | |
| 15 | 5-chloro-3-phenoxytrifluoromethanesulfonanilide, m.p. 51—54°C. | 15 |
| | 5-chloro-2-phenoxytrifluoromethanesulfonanilide, m.p. 66.5—68°C. | |
| | 3-phenylsulfonitrifluoromethanesulfonanilide, m.p. 106—108°C. | |
| | 3-phenoxytrifluoromethanesulfonanilide, b.p. 128°C./0.05 mm. | |
| | 2-methyl-5-phenylthiotrifluoromethanesulfonanilide, m.p. 82—83.5°C. | |
| 20 | 4-chloro-3-phenylthiotrifluoromethanesulfonanilide, m.p. 83—85.5°C. | 20 |
| | 2-methyl-3-phenylthiotrifluoromethanesulfonanilide, m.p. 123.5—124.5°C. | |
| | 4-chloro-2-phenoxytrifluoromethanesulfonanilide, m.p. 78—81.5°C. | |
| | 3-chloro-2-phenoxytrifluoromethanesulfonanilide, m.p. 65.5—67.5°C. | |
| | 2-methyl-4-phenylthiotrifluoromethanesulfonanilide, m.p. 100.5—102°C. | |
| 25 | 2-(4-methoxyphenoxy)trifluoromethanesulfonanilide, m.p. 95—97°C. | 25 |
| | 2-phenoxytrifluoromethanesulfonanilide, m.p. 65—67.5°C. | |
| | 4-phenoxytrifluoromethanesulfonanilide, m.p. 78.5—80°C. | |
| | 2-methoxy-4-phenylthiotrifluoromethanesulfonanilide, m.p. 75.5—76.5°C. | |
| | 4-(4-nitrophenylthio)trifluoromethanesulfonanilide, m.p. 90—92°C. | |
| | 2-methyl-4-phenylthiotrifluoromethanesulfonanilide, m.p. 91—93°C. | |
| 30 | 2-phenylthiotrifluoromethanesulfonanilide, m.p. 41.5—44°C. | 30 |
| | 2-phenoxy-5-trifluoromethyltrifluoromethanesulfonanilide, m.p. 74.5—76.5°C. | |
| | 5-methyl-2-phenoxytrifluoromethanesulfonanilide, m.p. 65.5—68°C. | |
| | 3-chloro-2-phenylthiotrifluoromethanesulfonanilide, m.p. 63—63.5°C. | |
| 35 | 4-chloro-2-phenylthiotrifluoromethanesulfonanilide, m.p. 75—76.5°C. | 35 |
| | 5-chloro-2-phenylthiotrifluoromethanesulfonanilide, m.p. 42—44.5°C. | |
| | 2-phenylthio-5-trifluoromethyltrifluoromethanesulfonanilide, m.p. 63.5—65.5°C. | |
| | 5-methyl-2-phenylthiotrifluoromethanesulfonanilide, m.p. 54—55°C. | |
| | 2-(4-chlorophenylthio)trifluoromethanesulfonanilide, m.p. 74—76°C. | |
| 40 | 6-methyl-2-phenoxytrifluoromethanesulfonanilide, m.p. 79—81°C. | 40 |
| | 5-methoxy-2-phenoxytrifluoromethanesulfonanilide, m.p. 63—64°C. | |
| | 4-methyl-3-phenylthiotrifluoromethanesulfonanilide, m.p. 59.5—61.5°C. | |
| | 3-methyl-2-phenoxytrifluoromethanesulfonanilide, m.p. 68—70°C. | |
| | 3-(2-methoxyphenylthio)trifluoromethanesulfonanilide, b.p. 173—177°C./0.03 mm. | |
| 45 | 4-(3,4-dichlorophenylthio)trifluoromethanesulfonanilide, m.p. 91—94°C. | 45 |
| | 4-(3,4-dimethylphenylthio)trifluoromethanesulfonanilide | |
| | 4-(2,5-dichlorophenylthio)trifluoromethanesulfonanilide, m.p. 108—110°C. | |
| | 4-(2-methylphenylthio)trifluoromethanesulfonanilide, m.p. 55—57°C. | |
| 50 | 4-(3-methylphenylthio)trifluoromethanesulfonanilide, m.p. 32—35°C. | 50 |
| | 4-(4-methylphenylthio)trifluoromethanesulfonanilide, m.p. 72—74°C. | |
| | 4-(4-chlorophenylthio)trifluoromethanesulfonanilide, m.p. 88—90°C. | |
| | 4-(4-bromophenylthio)trifluoromethanesulfonanilide, m.p. 97—99°C. | |
| | 4-(4-bromo-3-methylphenylthio)trifluoromethanesulfonanilide, m.p. 70—72°C. | |
| | 4-(4- <i>t</i> -butylphenylthio)trifluoromethanesulfonanilide | |
| 55 | 4-(3-methoxyphenylthio)trifluoromethanesulfonanilide, m.p. 56—59°C. | 55 |
| | 4-(4-methoxyphenylthio)trifluoromethanesulfonanilide, m.p. 79—84°C. | |
| | 4-(2,4-dimethylphenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 85—92°C. | |
| | 4-(2,5-dichlorophenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 138—140°C. | |
| 60 | 3-methyl-4-phenylthiotrifluoromethanesulfonanilide, m.p. 79—81°C. | 60 |
| | 3-chloro-4-phenylthiotrifluoromethanesulfonanilide, m.p. 84—87°C. | |
| | 2-methyl-4-(2-methylphenylthio)trifluoromethanesulfonanilide, m.p. 112—114°C. | |
| | 2-methyl-4-(4-methylphenylthio)trifluoromethanesulfonanilide, m.p. 105—107°C. | |

4-(4-chlorophenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 92—93°C.
 4-(4-bromophenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 91—94°C.
 4-(4-bromo-3-methylphenylthio)-2-methyltrifluoromethanesulfonanilide,
 m.p. 104—105°C.

5

4-(3-methoxyphenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 69—72°C.
 4-(4-methoxyphenylthio)-2-methyltrifluoromethanesulfonanilide, m.p. 109—112°C.
 2-methyl-4-(3-methylphenylthio)trifluoromethanesulfonanilide, m.p. 82—84°C.

5

The following compounds are prepared from the reaction of the corresponding compound of Formula II and the corresponding fluoroalkanesulfonyl fluoride or chloride according to Method A. The acid acceptor and solvent used are also noted.

10

10

TABLE I

Halide	Acid Acceptor	Solvent	Product	Boiling Point (in °C/mm.) or Melting Point (in °C.)
Fluoride	Triethyl- amine	None	3-phenoxyper- fluorobutane- sulfonanilide	155/0.02
Fluoride	Triethyl- amine	None	3-phenylthio- perfluorobutane- sulfonanilide	158/0.08
Chloride	Dimethyl- aniline	Chloro- form	3-phenoxydi- fluoromethane- sulfonanilide	36—38
Chloride	Dimethyl- aniline	Chloro- form	3-phenylthiodi- fluoromethane- sulfonanilide	81—83

Examples 2, 3 and 4 relate respectively to the preparation of compounds of Formula I by Methods B 1., B 2. and B 3.

Example 2

15

A slurry of 4-bromotrifluoromethanesulfonanilide (15 g., 0.05 mole), cuprous thiophenolate (10 g., 0.058 mole), sodium bicarbonate (10 g.) and dimethylformamide (100 ml.) is heated at 145 to 150°C. for 2.5 days. The reaction mixture is poured in water (2 liters), the yellow by-product is removed by filtration and the water is acidified to give an oil. This oil is distilled to yield 4-phenylthiotrifluoromethanesulfonanilide, b.p. 159—163°C./0.5 mm.

15

20

20

Analysis:

Calculated for: $C_{13}H_{10}F_3NO_2S_2$: C, 46.8; H, 3.0; N, 4.2

Found: C, 46.3; H, 2.9; N, 4.3

25

The following compounds are prepared using Method B 1. specifically exemplified in Example 2.

25

3-(4-chlorophenylthio)trifluoromethanesulfonanilide, m.p. 92.5—94.5

3-(4-fluorophenylthio)trifluoromethanesulfonanilide, b.p. 157—162°C./0.03 mm.

3-(3-methylphenylthio)trifluoromethanesulfonanilide, b.p. 156—160°C./0.05 mm.

30

3-nitro-4-phenylthiotrifluoromethanesulfonanilide, isolated as the triethylammonium salt, m.p. 110—112°C.

30

3-(2-methylphenylthio)trifluoromethanesulfonanilide, b.p. 150—158°C./0.05 mm.

Example 3

35

A suspension of 2-chloro-5-aminotrifluoromethanesulfonanilide (26 g., 0.085 mole) in water (40 ml.) and concentrated hydrochloric acid (15 ml.) is heated on a steam bath for one hour. More hydrochloric acid (15 ml.) is added and the solution is chilled to 0 to 5°C. Sodium nitrite (6 g., 0.085 mole) dissolved in a minimum amount of water is added while maintaining the temperature below 5°C.

35

A solution of sodium hydroxide (8.6 g.) in water (70 ml.) is heated to 110°C. under a nitrogen atmosphere and thiophenol (18.7 g.) is added. The cold diazonium salt solution is added over one hour, the mixture is stirred an additional thirty minutes, then made basic with sodium hydroxide solution. This solution is extracted with chloroform, acidified with concentrated hydrochloric acid and then extracted with dichloromethane. The dichloromethane extracts are dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. The solid 2-chloro-5-phenylthiotrifluoromethanesulfonanilide is recrystallized twice from benzene and dried, m.p. 66—68°C.

Analysis:

Calculated for $C_{13}H_6ClF_3NO_2S_2$: C, 42.5; H, 2.5; N, 3.8
Found: C, 42.9; H, 2.6; N, 4.0

Example 4

A solution of potassium hydroxide (12.3 g., 0.22 mole), 2-chloro-5-nitrotrifluoromethanesulfonanilide (15.3 g., 0.05 mole), phenol (1.2 g., 0.05 mole), pyridine (25 ml.) and benzene (50 ml.) is stirred and heated, removing water by means of a Dean-Stark trap. After all benzene is distilled out more pyridine (25 ml.) is added and the mixture is heated to 150°C. A small amount of cuprous chloride is added and heating is continued for several hours. The mixture is poured into water, treated with decolorizing charcoal then acidified. The organic layer is separated and distilled. The fraction boiling at 185—195°C./0.3 mm. is solidified by scratching, recrystallized twice from hexanetoluene, once from hexanetrichloroethylene to give 5-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 85—87.5°C.

Analysis:

	%C	%H	%N
Calculated for $C_{13}H_6F_3N_2O_5S_2$:	43.0	2.5	7.7
Found:	43.0	2.4	7.8

The following compounds are prepared using the Method B 3 specifically exemplified in Example 4.

5-nitro-2-phenylthiotrifluoromethanesulfonanilide, m.p. 98—100°C.

3-nitro-4-phenoxytrifluoromethanesulfonanilide, isolated as the triethylammonium salt, m.p. 72—74°C.

Examples 5 and 6 relate to the preparation of compounds of Formula I by Method C.

Example 5

3-Phenylthiotrifluoromethanesulfonanilide (16.7 g., 0.050 mole) and acetone (25 ml.) cooled to -6 to -2°C. are treated with 30 percent hydrogen peroxide (5.2 ml., 50.8 mmole) in acetone (15 ml.) during ninety minutes. The mixture is stirred until its temperature is about 25°C., and the acetone is removed *in vacuo*. Benzene is added, then removed *in vacuo* to azeotrope off any water residue to give an oil. The oil is chromatographed on a "Florisil" (Trade Mark) column, eluting first with 1:1 benzene:trichloroethylene, then 1:1 benzene:dichloromethane and finally with acetone. The fraction eluting with acetone is dissolved in 10 percent sodium hydroxide solution. This solution is extracted with diethyl ether and the ether extracts are discarded. The solution is then acidified to provide a white gum which is extracted with diethyl ether. The ether layer is dried over magnesium sulfate, the solvent is removed *in vacuo* and the 3-phenylsulfonyltrifluoromethanesulfonanilide is recrystallized from a trichloroethylene-cyclohexane mixture, then twice from cyclohexane to give a white solid, m.p. 109.5—111°C.

Analysis:

Calculated for $C_{15}H_{10}F_3NO_5S_2$: C, 44.8; H, 2.9; N, 4.0
Found: C, 44.5; H, 3.0; N, 3.9

The following compounds are prepared using the general Method C specifically exemplified in Example 5.

3-phenylsulfonylperfluoroethanesulfonanilide

2-phenylsulfonyl trifluoromethanesulfonanilide, m.p. 87—89°C.

4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 121—123°C.

2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 138—139.5°C.

2-methyl-5-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 113—115°C.

4-(4-acetamidophenylsulfonyl)trifluoromethanesulfonanilide, m.p. 233.5—235°C.

	4-(4-acetamidophenylsulfinyl)trifluoromethanesulfonanilide, m.p. 202.5—204.5°C.	
	2-methoxy-4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 117.5—119°C.	
	2-methoxy-4-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 124—216°C.	
	4-(4-nitrophenylsulfonyl)trifluoromethanesulfonanilide, m.p. 178.5—180.5°C.	
5	4-(2-methylphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 157—160°C.	5
	4-(2-methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 101—108°C.	
	4-(3-methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 168—173°C.	
	4-(4-methylphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 180—182°C.	
	4-(4-methylphenylsulfonyl)trifluoromethanesulfonanilide; m.p. 172—175°C.	
10	4-(4-chlorophenylsulfinyl)trifluoromethanesulfonanilide, m.p. 189—192°C.	10
	4-(4-chlorophenylsulfonyl)trifluoromethanesulfonanilide, m.p. 165—169°C.	
	4-(4-bromophenylsulfinyl)trifluoromethanesulfonanilide, m.p. 196—199°C.	
	4-(4-bromophenylsulfonyl)trifluoromethanesulfonanilide, m.p. 186—189°C.	
15	4 - (4 - bromo - 3 - methylphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 154—160°C.	15
	4 - (4 - bromo - 3 - methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 173—178°C.	
	4-(4- <i>t</i> -butylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 219—223°C.	
	4-(4-methoxyphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 169—172°C.	
20	4-(4-methoxyphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 178—181°C.	20
	4 - (2,4 - dimethylphenylsulfonyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 157—159°C.	
	4 - (2,5 - dichlorophenylsulfonyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 167—174°C.	
25	3-methyl-4-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 180—183°C.	25
	3-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 113—116°C.	
	3-chloro-4-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 154—157°C.	
	3-chloro-4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 120—124°C.	
30	2 - methyl - 4 - (2 - methylphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 146—150°C.	30
	2 - methyl - 4 - (2 - methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 132—138°C.	
	2 - methyl - 4 - (3 - methylphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 119—122°C.	
35	2 - methyl - 4 - (3 - methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 110—114°C.	35
	2 - methyl - 4 - (4 - methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 170—173°C.	
40	4 - (4 - chlorophenylsulfinyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 119—123°C.	40
	4 - (4 - chlorophenylsulfonyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 140—142°C.	
	4 - (4 - bromophenylsulfinyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 147—154°C.	
45	4 - (4 - bromophenylsulfonyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 149—153°C.	45
	4 - (4 - bromo - 3 - methylphenylsulfonyl) - 2 - methyltrifluoromethanesulfonanilide, m.p. 163—166°C.	
50	3-(2-methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 57—62°C.	50
	3-(4-methylphenylsulfonyl)trifluoromethanesulfonanilide, m.p. 115—119°C.	
	3-(4-chlorophenylsulfonyl)trifluoromethanesulfonanilide, m.p. 134—140°C.	

Example 6

55	To a stirred solution of 4-phenylthiotrifluoromethanesulfonanilide (8.2 g., 0.0246 mole), prepared according to Example 8, and 10 percent sodium hydroxide solution (8.93 ml.) is added sodium metaperiodate (5.27 g., 0.0246 mole). The sodium metaperiodate is washed in with water (140 ml.), and the mixture is stirred for one and one-half hours. Enough 10% sodium hydroxide is added to maintain the solution at a basic pH. The mixture is filtered, then the filtrate is acidified, extracted with chloroform and dried over magnesium sulfate. The solution is filtered and the solvent evaporated <i>in vacuo</i> . The solid 4-phenylsulfinyltrifluoromethanesulfonanilide is recrystallized from isopropyl ether-isopropanol with treatment with decolorizing charcoal to yield an off-white powder, m.p. 164—166°C.	55
60		60

Analysis:

Calculated for $C_{13}H_{10}F_3NO_3S_2$: C, 44.7; H, 2.9; N, 4.0

Found: C, 45.0; H, 3.0; N, 4.0

The following compounds are prepared using the general Method C specifically exemplified in Example 6.

3-(2-methoxyphenylsulfinyl)trifluoromethanesulfonanilide, m.p. 176.5—178.5°C.

2-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 128—130°C.

3-(4-chlorophenylsulfinyl)trifluoromethanesulfonanilide, m.p. 117—119°C.

N-methyl-3-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 83—84.5°C.

4-(4-nitrophenylsulfinyl)trifluoromethanesulfonanilide, m.p. 205.5—207°C.

2-methyl-4-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 116—120°C.

2-methyl-5-phenylsulfinyltrifluoromethanesulfonanilide, m.p. 118.5—122.5°C.

Examples 7—11 relate to the preparation of compounds of Formula I by Method D.

Example 7

4-Phenylthiotrifluoromethanesulfonanilide (17.8 g., 0.056 mole) is dissolved in acetic acid (125 ml.), sodium acetate (4.6 g., 0.056 mole) is added then bromine (8.95 g., 0.056 mole) is added over five minutes. After stirring one hour the mixture is heated on a steam bath one-half hour, then poured into water (750 ml.). The solid product is recovered by filtration, dissolved in dichloromethane and dried over magnesium sulfate. The solvent is evaporated *in vacuo*, and the residue dissolved in a benzene-hexane mixture. Triethylamine (excess) is added and the solid product is isolated by filtration, then recrystallized twice from isopropanol, giving triethylammonium 2-bromo-4-phenylthiotrifluoromethanesulfonanilide, m.p. 92—94°C.

Analysis:

Calculated for $C_{13}H_9BrF_3NO_2S_2 \cdot C_6H_{15}N$: %C 44.4 %H 4.7 %N 5.45

Found: 45.1 4.9 5.5

Example 8

3-(2-Methoxyphenylthio)trifluoromethanesulfonanilide (16.5 g., 0.045 mole) is placed in glacial acetic acid (65 ml.) and the mixture is heated to reflux temperature (about 130°C.). Excess hydroiodic acid (57%, 66 ml.) is added and the mixture is maintained at its reflux temperature for 6 hours, then stirred about 70 hours at room temperature. The mixture is diluted with water, then extracted with dichloromethane. The dichloromethane extracts are combined and dried over magnesium sulfate, then the solvent is removed *in vacuo*. The solid residue is recrystallized from a mixture of hexane and benzene to give white crystals of 3-(2-hydroxyphenylthio)trifluoromethanesulfonanilide, m.p. 115—116.5°C.

Analysis:

Calculated for $C_{13}H_{10}F_3NO_3S_2$: %C 44.7 %H 2.9 %N 4.0

Found: 44.5 2.9 4.0

The following compounds are prepared using the method of Example 8.

3-(4-hydroxyphenoxy)trifluoromethanesulfonanilide, b.p. 215—217/0.5 mm.

5-hydroxy-2-phenoxytrifluoromethanesulfonanilide, m.p. 94—96°C.

Example 9

5-Nitro-2-phenoxytrifluoromethanesulfonanilide (12.4 g., 0.0342 mole) in ethanol is reduced over palladium on charcoal at about 45 psi. After hydrogen uptake is complete the mixture is filtered, then the filtrate is evaporated *in vacuo* to a solid which is sublimed to give white solid 5-amino-2-phenoxytrifluoromethanesulfonanilide, m.p. 120.5—123°C.

Analysis:

Calculated for $C_{13}H_{11}F_3N_2O_3S_2$: %C 47.0 %H 3.3

Found: 47.0 3.4

The following compounds are prepared using the method of Example 9, or alternatively Raney nickel may be used as the reduction catalyst.

4-(4-aminophenylthio)trifluoromethanesulfonanilide, m.p. 116.5—118°C.

5-amino-2-phenylthiotrifluoromethanesulfonanilide, m.p. 103—106°C.

4-amino-2-phenoxytrifluoromethanesulfonanilide, isolated as the sodium salt, m.p. 205—207°C.

3-amino-4-phenylthiotrifluoromethanesulfonanilide, isolated as the triethylammonium salt, m.p. 106—108.5°C.

5 4-amino-2-phenylthiotrifluoromethanesulfonanilide, isolated as the triethylammonium salt, m.p. 128—130°C. 5

Example 10

10 5-Amino-2-phenoxytrifluoromethanesulfonanilide (1.5 g., 4.5 mmole) is dissolved in glacial acetic acid and treated with excess acetic anhydride (about 0.5 g.) and the solution is stirred two hours. The solution is poured into water and the solid product is isolated by filtration, dissolved in ethanol and treated with decolorizing charcoal. The ethanol is evaporated *in vacuo*, then recrystallized from a chloroform-toluene-hexane mixture to give a tan solid, 5-acetamido-2-phenoxytrifluoromethanesulfonanilide, m.p. 184—186°C. 10

15 Analysis:
Calculated for $C_{15}H_{11}F_3N_2O_4S$: %C 48.1 %H 3.5 %N 7.5
Found: 47.8 3.5 7.8 15

The following compounds are prepared using the method of Example 10.

4-(4-acetamidophenylthio)trifluoromethanesulfonanilide, m.p. 185.5—187°C.

20 3-acetamido-4-phenylthiotrifluoromethanesulfonanilide, m.p. 179—182.5°C. 20

2-acetamido-4-phenylthiotrifluoromethanesulfonanilide, m.p. 185.5—187°C.

Example 11

25 4-Phenylthiotrifluoromethanesulfonanilide is dissolved in glacial acetic acid and treated with an equimolar amount of 70 percent nitric acid. The mixture is stirred one hour, then poured in water. The solid product is collected by filtration and recrystallized from ethanol to give 2-nitro-4-phenylthiotrifluoromethanesulfonanilide, m.p. 105.5—107°C. 25

30 Analysis:
Calculated for $C_{13}H_8F_3N_2O_4S_2$: %C 41.25 %H 2.4 %N 7.4
Found: 41.2 2.4 7.4 30

The following compounds are prepared using the method of Example 11:

2-(4'-Chlorophenoxy)-4-nitrotrifluoromethanesulfonanilide, m.p. 129—130°C.

5-chloro-4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 123—125°C.

35 5-methyl-4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 97—99°C. 35

5-methoxy-4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 133—135°C.

4-nitro-2-phenoxydifluoromethanesulfonanilide, m.p. 92—94°C.

4-nitro-2-phenylthiotrifluoromethanesulfonanilide, m.p. 69—70.5°C.

Examples 12—15 relate to the preparation of the preparation of compounds of Formula I by Method E.

Example 12

40 Sodium-2-methyl-4-phenylsulfonyl trifluoromethanesulfonanilide in acetone is combined with an equimolar amount of ethyl chloroformate and the mixture is stirred at room temperature overnight. The mixture is filtered and the filtrate evaporated *in vacuo* to give N-ethoxycarbonyl-2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 118—120°C. 45

The following compounds are prepared using the method of Example 12.

N-ethoxycarbonyl-3-phenoxytrifluoromethanesulfonanilide, b.p. 175°C./0.1 mm.

N-ethoxycarbonyl-2-methyl-4-phenylthiotrifluoromethanesulfonanilide, m.p. 63—64.5°C.

Example 13

50 3-Phenoxytrifluoromethanesulfonanilide is dissolved in acetone, treated with an equimolar amount of sodium carbonate and stirred one hour. Excess methyl iodide is added and the mixture is stirred overnight. The mixture is filtered and the filtrate evaporated *in vacuo*. The residue is extracted with a mixture of chloroform and water, then the chloroform layer is dried over anhydrous magnesium sulfate. The chloroform is evaporated *in vacuo* to give a residue which is distilled. The product, N-methyl-3-phenoxytrifluoromethanesulfonanilide, boils at 124—126°C./0.05 mm. 55

The following compound is prepared using the method of Example 13.
N-methyl-3-phenylthiotrifluoromethanesulfonanilide, b.p. 150°C./0.05 mm.

Example 14

Sodium 2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide is dissolved in 1,2-dimethoxyethane by gentle heating. An equimolar amount of cyanogen bromide is dissolved in a small amount of 1,2-dimethoxyethane and added to the warm solution. The mixture is heated to its reflux temperature and maintained there for one hour. The mixture is filtered and the filtrate evaporated *in vacuo* to give the desired product, N - cyano - 2 - methyl - 4 - phenylsulfonyltrifluoromethanesulfonanilide, m.p. 89—90.5°C.

Example 15

Sodium 2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide in acetone is stirred while adding an equimolar amount of methanesulfonyl chloride, and stirring is continued overnight. The mixture is filtered, and the filtrate is evaporated *in vacuo*. The residue is dissolved in dichloromethane, then washed with dilute sodium hydroxide and finally in water. The product, N-methanesulfonyl-2-methyl-4-phenylsulfonyltrifluoromethanesulfonanilide, is recovered by evaporation of the dichloromethane followed by elution chromatography of the product, an oil.

Examples 16 and 17 relate to the preparation of salts according to Formula I from the acid-form compounds.

Example 16

The preparation of triethylammonium 3-phenoxyperfluoroethanesulfonanilide.

Crude 3-phenoxyperfluoroethanesulfonanilide (4.7 g., 0.10 mole), prepared from perfluoroethanesulfonyl fluoride and 3-phenoxyaniline by Method A, diisopropyl ether (50 ml.) and triethylamine (20.2 g., 0.20 mole) are stirred for six hours at room temperature, the solution is filtered and the salt is isolated by removing the volatiles *in vacuo*. The product is triethylammonium 3-phenoxyperfluoroethanesulfonanilide, which is recrystallized from a diisopropyl ether-isopropanol mixture, m.p. 80.5—82.5°C.

Analysis:

Calculated for $C_{14}H_{19}F_5NO_3S_2$: C, 51.3; H, 5.4; N, 6.0
Found: C, 51.4; H, 5.4; N, 5.8

Using the procedure of Example 16 the following compounds are prepared:

triethylammonium 5 - amino - 2 - phenoxytrifluoromethanesulfonanilide, m.p. 130—134°C.

triethylammonium 3-phenylthioperfluoroethanesulfonanilide, m.p. 78.5—81.5°C.

triethylammonium 2 - (4 - chlorophenoxy)trifluoromethanesulfonanilide, m.p. 78—84°C.

triethylammonium 5 - amino - 2 - phenoxydifluoromethanesulfonanilide, m.p. 70—120°C. (d.)

triethylammonium 5 - nitro - 2 - phenoxydifluoromethanesulfonanilide, m.p. 70—74°C.

triethylammonium 4 - phenylthio - 2 - trifluoromethyltrifluoromethanesulfonanilide, m.p. 88—92°C.

triethylammonium 5 - chloro - 2 - (2,4 - dichlorophenoxy)trifluoromethanesulfonanilide, m.p. 127—129°C.

Example 17

3-Phenylsulfonylperfluoroethanesulfonanilide is dissolved in acetone and treated with an equimolar amount of sodium carbonate. The solution is stirred overnight, then filtered and evaporated to dryness to give a white solid. The product, sodium 3-phenylsulfonylperfluoroethanesulfonanilide, is recrystallized from isopropanol and found to melt higher than 300°C.

Analysis:

Calculated for $C_{14}H_9F_5NNaO_4S_2$: %C 38.4 %H 2.1
Found: 38.5 2.3

The following compound is prepared using the method of Example 17.
sodium 4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 281—282°C.

The following additional compounds of the invention are also prepared utilizing one or another of the preceding processes:

Name	Melting Point (in °C.)
4-(1-naphthylthio)trifluoromethanesulfonanilide	74—76
4-(1-naphthylsulfonyl)trifluoromethanesulfonanilide	176—179
4-(3-methoxyphenylsulfinyl)trifluoromethanesulfonanilide	130—133
4-(3-methoxyphenylsulfonyl)trifluoromethanesulfonanilide	161—163
4-(3,4-dichlorophenylsulfinyl)trifluoromethanesulfonanilide	164—168
4-(3,4-dichlorophenylsulfonyl)trifluoromethanesulfonanilide	176—180
4-(2,5-dichlorophenylsulfinyl)trifluoromethanesulfonanilide	188—192
4-(2,5-dichlorophenylsulfonyl)trifluoromethanesulfonanilide	164—180
4-(4-bromo-3-methylphenylsulfinyl)-2-methyltrifluoromethanesulfonanilide	133—136
4-(4-bromo-3-methylphenylsulfonyl)-2-methyltrifluoromethanesulfonanilide	163—166
4-(4- <i>t</i> -butylphenylthio)-2-methyltrifluoromethanesulfonanilide	101—104
4-(4- <i>t</i> -butylphenylsulfinyl)-2-methyltrifluoromethanesulfonanilide	157—165
4-(4- <i>t</i> -butylphenylsulfonyl)-2-methyltrifluoromethanesulfonanilide	189—193
3-(2,4-dimethylphenylthio)trifluoromethanesulfonanilide	160—162°/0.1mm
3-(2,4-dimethylphenylsulfinyl)trifluoromethanesulfonanilide	115—122
3-(2,4-dimethylphenylsulfonyl)trifluoromethanesulfonanilide	106—111
3-(1-naphthylthio)trifluoromethanesulfonanilide	172—180°/0.18mm
3-(1-naphthylsulfinyl)trifluoromethanesulfonanilide	143—149
3-(1-naphthylsulfonyl)trifluoromethanesulfonanilide	134—142

Name	Melting Point (in °C.)
3-(3,4-dichlorophenylthio)trifluoromethanesulfonanilide	174—176°/0.8
3-(2-naphthylthio)trifluoromethanesulfonanilide	67.5—71
3-(2-naphthylsulfinyl)trifluoromethanesulfonanilide	180—187
3-(2-naphthylsulfonyl)trifluoromethanesulfonanilide	175—178
3-(4-fluorophenylsulfinyl)trifluoromethanesulfonanilide	92—94
3-(4-fluorophenylsulfonyl)trifluoromethanesulfonanilide	108—112
3-(2-methylphenylsulfinyl)trifluoromethanesulfonanilide	114—120
3-(3-methylphenylsulfinyl)trifluoromethanesulfonanilide	98—101
3-(3-methylphenylsulfonyl)trifluoromethanesulfonanilide	92—94
3-(4-methylphenylsulfinyl)trifluoromethanesulfonanilide	103—104
4-(4- <i>t</i> -butylphenylsulfinyl)trifluoromethanesulfonanilide	183—186
4-(1-naphthylsulfinyl)trifluoromethanesulfonanilide	175—178
2-methyl-4-(2-naphthylthio)trifluoromethanesulfonanilide	116—117
2-methyl-4-(2-naphthylsulfinyl)trifluoromethanesulfonanilide	165—173
2-methyl-4-(2-naphthylsulfonyl)trifluoromethanesulfonanilide	165—167
2-methyl-4-(1-naphthylthio)trifluoromethanesulfonanilide	115—119
2-methyl-4-(1-naphthylsulfinyl)trifluoromethanesulfonanilide	205—209
2-methyl-4-(1-naphthylsulfonyl)trifluoromethanesulfonanilide	190—195
4-(3-methoxyphenylsulfinyl)-2-methyltrifluoromethanesulfonanilide	138—140
4-(3-methoxyphenylsulfonyl)-2-methyltrifluoromethanesulfonanilide	135—137

Name	Melting Point (in °C.)
4-(4-acetamidophenylthio)-2-methyltrifluoromethanesulfonanilide	153—154
4-(2,4-dimethylphenylsulfinyl)-2-methyltrifluoromethanesulfonanilide	157—160
4-(2,5-dichlorophenylsulfinyl)-2-methyltrifluoromethanesulfonanilide	156—160
3-(3-methoxyphenylthio)trifluoromethanesulfonanilide	180—185°/10.4mm
3-(3-methoxyphenylsulfonyl)trifluoromethanesulfonanilide	83—88
4-phenylthio-3-trifluoromethyltrifluoromethanesulfonanilide	75—78
4-(2,5-dimethylphenylthio)trifluoromethanesulfonanilide	163—165°/0.5mm
4-(2,5-dimethylphenylsulfinyl)trifluoromethanesulfonanilide	164—168
4-(2,5-dimethylphenylsulfonyl)trifluoromethanesulfonanilide	158—161

Examples 18—22 relate to the preparation of precursors of compounds of Formula I.

Example 18

5 Under a nitrogen atmosphere a mixture of 2-chlorophenol (26.0 g., 0.202 mole),
pyridine (25 ml.) and benzene (50 ml.) is heated to rapid reflux and treated with 0.20
equivalents of aqueous potassium hydroxide. Water is removed by azeotropic distilla-
10 tion for a period of three hours. The benzene is then removed by distillation, the
solution is cooled below its boiling point and 3-bromonitrobenzene (40.4 g., 0.20 mole)
and cuprous chloride 2.0 g.) are added. The mixture is then heated for 20 hours at
160°C., then mixed with 10 percent hydrochloric acid. This mixture is extracted with
dichloromethane, and the organic layer is fractionally distilled to give 2-chloro-3'-
nitrodiphenyl ether, b.p. 176—182/0.75 mm.

15 Using the method of Example 18, the following compounds are also prepared:
2,3-dimethyl-3'-nitrodiphenyl ether, b.p. 160—162°C./0.3 mm.
4-chloro-3'-nitrodiphenyl ether, b.p. 165—178°C./0.65 mm.
3-chloro-3'-nitrodiphenyl ether, b.p. 160—180°C./0.6 mm.
4-methoxy-3'-nitrodiphenyl ether, b.p. 165°C./0.6 mm.
20 3-trifluoromethyl-3'-nitrodiphenyl ether, b.p. 140°C./0.11 mm.

Example 19

Freshly distilled thiophenol (24.8 g., 0.225 mole) and cuprous oxide (14.95 g.,
0.10 mole as 96 percent active) are mixed under nitrogen atmosphere and refluxed in
95 percent ethanol (250 ml.) overnight. The bright yellow solid is filtered, separated
from cuprous oxide and dried.

25 Cuprous thiophenolate (17.25 g., 0.10 mole) is dissolved with 3-bromonitrobenzene
(20.2 g., 0.10 mole) in quinoline (100 ml.) and pyridine (20 ml.) and heated (under
a nitrogen atmosphere) for one hour at 150°C. and two hours at 165—170°C. The
mixture is cooled, then poured into aqueous hydrochloric acid (160 ml. concentrated
hydrochloric acid, 600 ml. water) and stirred two hours. The aqueous layer is decanted
30 and extracted with diethyl ether (2 × 150 ml.). The ether layers are washed with 10
percent hydrochloric acid, water, concentrated ammonium hydroxide and water, then
dried over magnesium sulfate. Fractional distillation yields 3-nitrodiphenylsulfide
(150—180°C./0.7 mm.), which solidifies on scratching when suspended in petroleum
ether.

Example 20

A mixture of 2-methyl-5-nitroaniline (76.1 g., 0.50 mole) concentrated hydrochloric acid (75 ml.) and water (200 ml.) is heated briefly on a steam bath and an additional portion of hydrochloric acid (75 ml.) is added. This solution is cooled to and maintained at 0 to 5°C. and treated with sodium nitrite (35.5 g., 0.50 mole).

A solution of sodium hydroxide (50 g., 1.25 mole) in water (300 ml.) is heated to 90°C. under a nitrogen atmosphere and thiophenol (110 g., 1.0 mole) is added. This solution is treated with the solution of the diazonium compound in 20 ml. portions over a period of one hour. Finally the mixture is maintained at 90°C. for one hour, then acidified with hydrochloric acid. The solution is steam distilled, the residue is extracted with dichloromethane and the 2-methyl-5-nitrodiphenylsulfide is separated by fractional distillation b.p. 148°C./0.15 mm. When recrystallized twice from hexane its m.p. is 65.5—68°C.

Example 21

A mixture of aluminum chloride (29.4 g., 0.22 mole) and benzene (250 ml.) is treated at reflux with 3-nitrobenzenesulfonyl chloride (44.3 g., 0.250 mole) in benzene (50 ml.) over a period of thirty minutes. After eighty minutes additional aluminum chloride (9 g.) is added. After an additional ninety minutes the mixture is cooled, then poured into a hydrochloric acid-ice mixture. This mixture is extracted with dichloromethane and the dichloromethane is then removed *in vacuo*. The solid 3-nitrodiphenylsulfone is a pale yellow solid after recrystallization from ethanol, m.p. 77—79°C.

Example 22

Crude 3-nitrodiphenylsulfide (4.6 g., 0.2 mole, 96 percent) is heated at 40°C. with Raney nickel (10 g.) under a hydrogen gas atmosphere (3 atm.) for sixteen hours in ethanol (200 ml.). Sulfur was added, the mixture was filtered and the ethanol removed *in vacuo*. The yellow oil distilled at 122°C./10—5 mm. to give 3-thiophenoxyaniline, which was suitable for use without further purification.

Example 23

The sodium salt of 5-amino-2-phenoxytrifluoromethanesulfonamide is reacted with ethyl chloroformate in acetone to provide a good yield of 5-(N-carbethoxyamino)-2-phenoxytrifluoromethanesulfonamide, as white needles, m.p. 116—117°C.

Analysis

	%C	%H
Calculated for $C_{16}H_{14}F_3N_2O_5S$:	47.6	3.7
Found:	47.4	3.7

Example 24

5-Amino-2-phenoxytrifluoromethanesulfonamide is reacted with formaldehyde and formic acid according to the well-known Eschweiler-Clarke reaction and 5-(N,N-dimethylamino)-2-phenoxytrifluoromethanesulfonamide, m.p. 127—135°C., is obtained.

Example 25

4-Methylthio-2-phenoxytrifluoromethanesulfonamide is oxidized using an excess of hydrogen peroxide in acetic acid on a steam bath. The product is precipitated by the addition of water then recrystallized from ethanol to give 4-methylsulfonyl-2-phenoxytrifluoromethanesulfonamide, m.p. 182—184°C.

Additional compounds of the invention which have been prepared using methods hereof are the following:

4-methylthio-2-phenoxytrifluoromethanesulfonamide, m.p. 82—84°C.

2-phenoxydifluoromethanesulfonamide, m.p. 57—58°C.

5 - acetamido - 4 - amino - 2 - phenoxytrifluoromethanesulfonamide, m.p. 189—190°C. (d.)

5-amino-2-(4-fluorophenoxy)trifluoromethanesulfonamide, isolated as the triethylammonium salt, m.p. 82—84.5°C.

4-amino-2-(4-chlorophenoxy)trifluoromethanesulfonamide, isolated as the triethylammonium salt, m.p. 130—140°C.

4-amino-5-chloro-2-phenoxytrifluoromethanesulfonamide, isolated as the triethylammonium salt, m.p. 128—133°C.

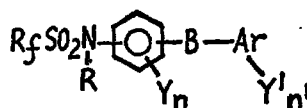
4-amino-5-methoxy-2-phenoxytrifluoromethanesulfonamide, isolated as the triethylammonium salt, m.p. 110—120°C.

4-amino-2-phenylsulfonyltrifluoromethanesulfonamide, isolated as the triethylammonium salt, decomposes above 150°C.

- 3-chloro-4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 101—102°C.
 5 - acetamido - 4 - nitro - 2 - phenoxytrifluoromethanesulfonanilide, m.p. 142.5—144.5°C.
 2-(4-fluorophenoxy)-5-nitrotrifluoromethanesulfonanilide, m.p. 95—97°C.
 4-nitro-3-phenoxytrifluoromethanesulfonanilide, m.p. 63—66°C. and 2-nitro-5-phenoxytrifluoromethanesulfonanilide, b.p. 155—160°C./0.1 mm are obtained as a mixture separable by fractional distillation.
 4-nitro-2-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 141—142°C.

WHAT WE CLAIM IS:—

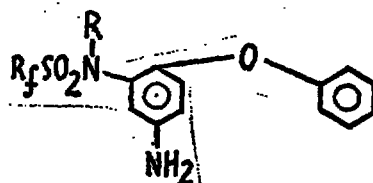
1. A fluoroalkylsulfonamidoaryl compound characterized by the formula



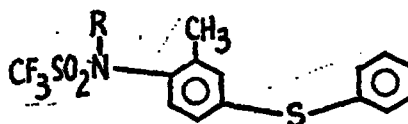
wherein R_f is a lower fluoroalkyl radical having at least two fluorine atoms bonded to the alpha carbon atom, R is hydrogen, cyano, alkyl, alkylsulfonyl, a cation or

$\text{—}\overset{\text{O}}{\parallel}\text{C—A—R'}$, where R' is alkyl and A is oxygen or a carbon-carbon bond, B is oxygen, sulfur, sulfinyl or sulfonyl, Ar is phenyl or naphthyl, the or each Y and the or each Y' is selected independently from halogen, alkyl, alkoxy, nitro, amino, alkanamido, haloalkyl, hydroxy, dialkylamino, carbalkoxamino, alkylthio, alkylsulfonyl, alkanoyl, dialkylsulfamoyl or alkylsulfinyl and n and n' are independently zero, one or two, provided that any individual aliphatic groups appearing in the R_f , R, R', Y and Y' moieties contain from one to four carbon atoms.

2. A compound according to claim 1 wherein R is hydrogen.
 3. A compound according to claim 1 wherein Ar is phenyl.
 4. A compound according to claim 1 wherein Ar is naphthyl.
 5. A compound according to claim 1 wherein R is a horticulturally acceptable cation.
 6. A compound according to claim 1 wherein R_f contains one carbon atom.
 7. A compound according to claim 1 wherein R_f is perfluoroalkyl.
 8. A compound according to claim 7 wherein R_f is trifluoromethyl.
 9. A compound according to claim 8 wherein R is hydrogen.
 10. A compound according to claim 8 wherein R is a cation.
 11. A compound according to claim 1 wherein B is oxygen.
 12. A compound according to claim 11 of the formula



13. 5-amino-2-phenoxytrifluoromethanesulfonanilide.
 14. A compound according to claim 1 wherein B is sulfur.
 15. A compound according to claim 14 of the formula



16. 2-methyl-4-phenylthiotrifluoromethanesulfonanilide.
 17. 2-Nitro-4-phenylthiotrifluoromethanesulfonanilide.
 18. A compound according to claim 1 wherein B is sulfinyl.



* C L M S *

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3-chloro-4-nitro-2-phenoxytrifluoromethanesulfonanilide, m.p. 101—102°C.
 5 - acetamido - 4 - nitro - 2 - phenoxytrifluoromethanesulfonanilide, m.p. 142.5—144.5°C.

5

2-(4-fluorophenoxy)-5-nitrotrifluoromethanesulfonanilide, m.p. 95—97°C.
 4-nitro-3-phenoxytrifluoromethanesulfonanilide, m.p. 63—66°C. and 2-nitro-5-phenoxytrifluoromethanesulfonanilide, b.p. 155—160°C./0.1 mm are obtained as a mixture separable by fractional distillation.
 4-nitro-2-phenylsulfonyltrifluoromethanesulfonanilide, m.p. 141—142°C.

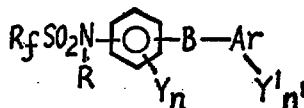
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WHAT WE CLAIM IS:—

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1. A fluoroalkylsulfonamidoaryl compound characterized by the formula

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wherein R_f is a lower fluoroalkyl radical having at least two fluorine atoms bonded to the alpha carbon atom, R is hydrogen, cyano, alkyl, alkylsulfonyl, a cation or

15

$\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{C} \text{---} \text{A} \text{---} \text{R}' \end{array}$, where R' is alkyl and A is oxygen or a carbon-carbon bond, B is oxygen, sulfur, sulfinyl or sulfonyl, Ar is phenyl or naphthyl, the or each Y and the or each Y' is selected independently from halogen, alkyl, alkoxy, nitro, amino, alkanamido, haloalkyl, hydroxy, dialkylamino, carbalkoxamino, alkylthio, alkylsulfonyl, alkanoyl, dialkylsulfamoyl or alkylsulfinyl and n and n' are independently zero, one or two, provided that any individual aliphatic groups appearing in the R_f , R, R' , Y and Y' moieties contain from one to four carbon atoms.

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20

2. A compound according to claim 1 wherein R is hydrogen.

3. A compound according to claim 1 wherein Ar is phenyl.

4. A compound according to claim 1 wherein Ar is naphthyl.

25

5. A compound according to claim 1 wherein R is a horticulturally acceptable cation.

25

6. A compound according to claim 1 wherein R_f contains one carbon atom.

7. A compound according to claim 1 wherein R_f is perfluoroalkyl.

8. A compound according to claim 7 wherein R_f is trifluoromethyl.

9. A compound according to claim 8 wherein R is hydrogen.

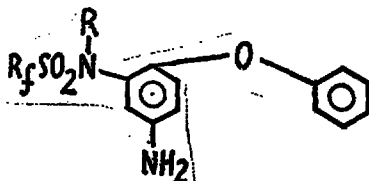
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10. A compound according to claim 8 wherein R is a cation.

30

11. A compound according to claim 1 wherein B is oxygen.

12. A compound according to claim 11 of the formula



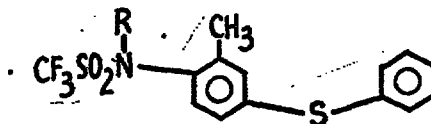
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13. 5-amino-2-phenoxytrifluoromethanesulfonanilide.

14. A compound according to claim 1 wherein B is sulfur.

35

15. A compound according to claim 14 of the formula



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16. 2-methyl-4-phenylthiotrifluoromethanesulfonanilide.

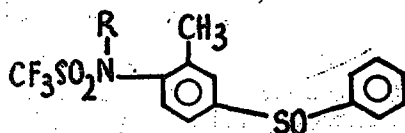
17. 2-Nitro-4-phenylthiotrifluoromethanesulfonanilide.

18. A compound according to claim 1 wherein B is sulfinyl.

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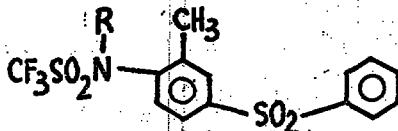
19. A compound according to claim 18 of the formula



20. 2-methyl-4-phenylsulfonyltrifluoromethanesulfonamide.

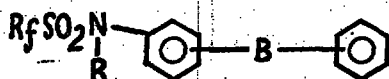
21. A compound according to claim 1 wherein B is sulfonyl.

22. A compound according to claim 21 of the formula



23. The compound 2-methyl-4-phenylsulfonyltrifluoromethanesulfonamide.

24. A compound according to claim 3 of the formula



25. A fluoroalkylsulfonamidoaryl compound substantially as herein described in any one of Examples 1 to 17 and 23 to 25.

26. A method for regulating the growth of higher plants which comprises contacting the said plants with an effective amount of a compound according to any of claims 1 to 25.

27. A composition for regulating the growth of higher plants which consists essentially of a compound according to any of claims 1 to 25 dispersed in an extending medium.

28. A method for regulating the growth of higher plants substantially as herein described.

29. A composition for regulating the growth of higher plants and substantially as herein described.

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