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(54) **METHOD FOR FUNCTIONALISING A DOUBLE BOND**

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(76) Inventor: **Nicolas Roques**, Lyon (FR)

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Correspondence Address:

Kevin E McVeigh

Intellectual Property Dept

Rhodia

259 Prospect Plains Road CN 7500

Cranbury, NJ 08512-7500 (US)

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(57) **ABSTRACT**

The invention concerns a method for functionalizing a double bond and, more particularly, a double bond bearing a metalloid atom. Said functionalization is produced by the action of perhalogenated sulphonyl chloride on the carbon bearing sulphur in the presence of a free radical initiator, preferably by homolytic cleavage. The invention is useful in organic synthesis.

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METHOD FOR FUNCTIONALISING A DOUBLE BOND

[0001] The present invention relates to a process for functionalizing a double bond, and more particularly a double bond bearing a metalloid atom. More particularly, the present invention is directed toward adding to a double bond, on the one hand, and to one of the atoms a halogen atom and, on the other hand, to the other carbon-based radical whose carbon atom is perhalogenated.

[0002] Compounds comprising perhalogenated and especially perfluoro carbon atoms play an increasingly important role in derivatives with biological activity, whether this biological activity is exerted in the animal kingdom or in the plant kingdom.

[0003] The synthesis or grafting of these perhalogenated and more preferentially perfluoro compounds is often difficult and requires expensive means.

[0004] Among the techniques that have been proposed is the one consisting in subjecting a double bond to the action of a sulfonyl halide. In particular, the action of trifluoromethanesulfonyl bromide has already been described in the Bulletin de la Societe Chimique de France, No. 6, 1986, from page 881 to page 884.

[0005] However, sulfonyl bromide is difficult and expensive to handle, especially on account of the high instability of this bromide. In addition, the bromide, like the chloride, is a powerful oxidizing agent which can modify the capacities for survival of the products obtained during this addition. The bromide ions formed during the reaction that react with the residual bromide can lead to bromine, which is then a source of further spurious reactions.

[0006] Trifluoromethanesulfonyl chloride, which is occasionally known as triflyl chloride, is significantly less reactive than the bromide; thus, it has been attempted to use very specific ruthenium complexes ($\text{Ru}(\text{P}\square_3\text{Cl}_2)$) to catalyze the addition to double bonds.

[0007] This addition appears to be relatively versatile, but the reactions are often difficult to reproduce and the results appear to be somewhat erratic.

[0008] It has also been proposed, in the case of double bonds bearing a silicon atom, to use free-radical generators such as tert-butyl peroxide.

[0009] One of the major risks of this technique lies in the fact that double bonds, under the action of free radicals, have a tendency to polymerize and not to lead to the addition reaction. Another risk is an oxidation with a chlorine according to a mechanism of positive chlorine type.

[0010] Thus, in the course of the study that led to the present invention, it has been possible to show that the action of sulfonyl chlorides on double bonds activated with an aromatic nucleus leads essentially to polymerization reactions rather than addition reactions.

[0011] In addition, certain double bonds, especially those that present major advantages for manufacturing synthons, are often not reactive enough to form the desired addition compounds.

[0012] It is thus seen that the decomposition of sulfonyl chlorides that are perhalogenated on the sulfur-bearing carbon

of the sulfonyl bonds does not give an addition reaction on a double bond with good results, except in an extremely limited number of already-functionalized products.

[0013] Accordingly, one of the aims of the present invention is to define a family of compounds bearing already-functionalized double bonds, that can give acceptable addition yields with a technique of decomposition of sulfonyl chloride initiated by free radicals.

[0014] Another aim of the present invention is to provide an optimization of the operating conditions for this novel family of compounds.

[0015] Another aim of the present invention is to provide a process that does not require expensive catalysts such as those based on metals from column VIII, especially of the platinum mine, and in particular ruthenium.

[0016] Another aim of the present invention is to provide a process in which ruthenium, especially in the form coordinated with phosphines and especially aromatic phosphines, is present in an amount such that the $[\text{Ru}]/[\text{sulfonyl chloride perhalogenated on the sulfur-bearing carbon}]$ molar ratio is not more than 1%, advantageously 0.1% and preferably 0.01%. It is even preferable for it not to be present.

[0017] Another aim of the present invention is to provide a process in which the platinum mine metals are present in an amount such that the $[\text{sum of the platinum mine metals}]/[\text{sulfonyl chloride perhalogenated on the sulfur-bearing carbon}]$ molar ratio is not more than 1%, advantageously 0.1% and preferably 0.01%. It is even preferable that they are not present.

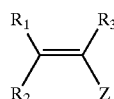
[0018] Another aim of the present invention is to provide a process in which the metals from column VIII are present in an amount such that the $[\text{sum of the metals from column VIII}]/[\text{sulfonyl chloride perhalogenated on the sulfur-bearing carbon}]$ molar ratio is not more than 1%, advantageously 0.16 and preferably 0.0%. It is even preferable for them not to be present.

[0019] Another aim of the present invention is to provide novel intermediates allowing novel synthetic routes.

[0020] The Periodic Table of the Elements used in the present patent application is that of the supplement to the Bulletin de la Société Chimique de France, January 1966, No. 1.

[0021] It may be useful to recall that the expression "identical or different" is used to indicate that the substituents under consideration may or may not be the same.

[0022] These aims and others which will become apparent hereinbelow are achieved by means of a process for functionalizing a double bond corresponding to formula I:



[0023] in which R_1 , R_2 and R_3 , which may be identical or different, are chosen from hydrogen and

hydrocarbyls attached to said double bond via a carbon of sp^3 hybridization;

[0024] in which Z is chosen from:

[0025] halogens, advantageously chlorine and fluorine;

[0026] residues such that ZH is an oxygenated acid;

[0027] radicals of formula $(CHR')_m-\Xi$ with Ξ chosen from halogens;

[0028] and radicals of formula $(CHR')_m-Y(O)_q-R_4$ in which

[0029] Y is a chalcogen, advantageously a light chalcogen;

[0030] q is zero or an integer not more than 3, advantageously not more than 2 and preferably not more than 1, with the condition that when Y is oxygen, q is equal to zero;

[0031] R' represents a hydrocarbyl, advantageously of not more than four carbons, or preferably a hydrogen;

[0032] m is equal to 1 or preferably to zero;

[0033] and R₄ is chosen from a hydrocarbyl or silyl group;

[0034] by the action of sulfonyl chloride perhalogenated on the sulfur-bearing carbon (of the sulfonyl function) in the presence of a free-radical initiator, preferably by homolytic cleavage.

[0035] The expression "perhalogenated carbon" should be understood as meaning a carbon of sp^3 nature optionally substituted with not more than two, and advantageously not more than one, electron-withdrawing group(s), and bearing no hydrogen, all the other atoms being halogens. It is preferable for these halogens borne by said perhalogenated carbon all to be chlorine or fluorine and preferably all fluorine.

[0036] It is important that the radicals R₁, R₃ and R₂, when they are hydrocarbyls (i.e. comprising hydrogen and carbon, but possibly comprising other atoms), are attached to the double bond via one of their sp^3 carbons, otherwise the reactivity toward the sulfonyl chloride is greatly affected thereby. In particular, the presence of an aromatic directly attached to the double bond plays an extremely unfavorable role. It is also recommended to avoid carbon atoms that are both allylic and benzylic. More generally, even when they are not conjugated with said double bond, the presence of an aromatic in the molecule is unfavorable. Thus, the presence of an aromatic in Z, especially when ZH is an oxygenated acid, is unfavorable especially when an aromatic nucleus is separated from a carbon of said double bond by less than two atoms of sp^3 hybridization (oxygen or carbon, preferably at least two sp^3 carbons). It should be noted that there is overlap between the definition of Z, $Z=(CHR')_m-Y(O)_q-R_4$ and that which indicates that Z is such that ZH is an oxygenated acid, especially when m is equal to zero, when q is equal to zero, when Y is oxygen and R₄ is a hydrocarbon radical attached to Y via an electron-withdrawing function such as, especially, carbonyl ($-CO-$), carbonate ($-CO-O-$), sulfonyl (SO_2), sulfoxide ($-SO-$), sulfate ($-SO_3-$

), phosphate $[P(=O)(-O-)O-]$, phosphonate $[P(=O)(-O-)-]$ and phosphinate $[P(=O)(-)-]$.

[0037] For reasons of steric bulk, it is recommended to choose the radicals R₁, R₃ and R₂ such that at least one and preferably two of these three radicals is hydrogen. It is also preferable that neither R₁ nor R₂ is tertiary. It is also preferable that at least one, and even both, of the radicals R₁ and R₂ are hydrogen.

[0038] It is preferable that the initiator generating the free radicals releases these radicals after a homolytic cleavage, i.e. a cleavage taking place between two atoms of the same element and generating an electron radical on each of the two atoms. This cleavage may be actinic, catalytic or, preferably, thermal.

[0039] The cleavage may also be heterolytic when systems are used involving metals that have two valency states (iron or copper) with peroxides and especially hydroperoxides.

[0040] Examples of preferred initiators that should be mentioned include various peroxides, preferably symmetrical, and various azo compounds, such as azobisisobutyronitrile (reference may be made especially to the "Polymer Handbook"). Among the peroxides, mention may be made of alkyl peroxides and especially tert-alkyl peroxides, and acyl peroxides, especially alkanoyl peroxides, that are preferably symmetrical.

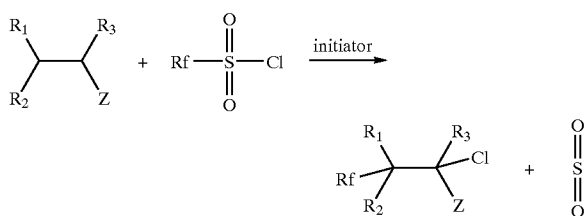
[0041] The acyl peroxides that may be used are preferably peroxides whose acyls are of low molecular weight, i.e. their carbon number is not more than 10, and preferably not more than 6 when they are aliphatic, but it is preferable to use acyl peroxides of aromatic nature, for instance benzoyl peroxide.

[0042] The free-radical initiator is advantageously not more than 0.2 times the molar amount of the sulfonyl chloride, preferably not more than 0.1 times, the optimum zone being between 1% and 8% of the amount of sulfonyl chloride. The reaction is advantageously conducted such that the release of the free radicals takes place gradually. A good technique for achieving this objective consists in adding the initiator, i.e. the free-radical generator, slowly and gradually. Another technique consists in using a temperature that allows the release of the free radicals to be controlled.

[0043] The reaction temperature is regulated such that it is between ambient temperature and 150° C., preferably between 50 and 120° C. and more preferentially between 60 and 100° C.

[0044] It should be noted that, for certain substrates, the reaction does not need an initiator, especially for substrates whose double bond bears a chalcogen, usually an oxygen. However, the use of a free-radical generator still improves the reaction yield.

[0045] The amount of substrate relative to the sulfonyl chloride is about once the molar amount. However, to satisfy specific problems, it is possible to depart considerably from this value which corresponds to the stoichiometric value as defined by the following reaction:



[0046] In particular, when there is a large risk of polymerization, a smaller amount of compounds bearing a double bond may be used relative to the amount of sulfonyl chloride. Thus, it is possible to vary very widely the ratio between the substrate bearing the double bond and the sulfonyl chloride. However, in the majority of cases, the ratio is of the order of 1 ± 0.5 .

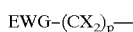
[0047] The pressure may vary within large proportions but it is preferable to work at an autogenous pressure or at atmospheric pressure.

[0048] Although its presence is not necessary, it is possible to use a solvent. The solvents that may be used are solvents that are inert toward sulfonyl chloride and that do not constitute free-radical traps.

[0049] Mention may thus be made of the hydrocarbons and halogenated derivatives that are usually used in free-radical chlorination reactions.

[0050] More specifically, alkanes with a suitable boiling point, i.e. whose boiling point is at least equal to the temperature at which it is desired to work; petroleum fractions; aromatic chloro derivatives, are all entirely acceptable.

[0051] The sulfonyl chlorides that are preferred are those corresponding to the formula $\text{R}_f\text{—SO}_2\text{—Cl}$ in which R_f corresponds to formula (IV):



[0052] in which:

[0053] the radicals X, which may be similar (i.e. they are identical) or different, represent a chlorine, a fluorine or a radical of formula $\text{C}_n\text{F}_{2n+1}$ with n being an integer not more than 5 and preferably not more than 2, with the condition that at least one of the radicals X is fluorine; when p is equal to 1,

[0054] EWG is an electron-withdrawing group (that is to say that the Hammett constant sigma p is >0 , advantageously at least equal to 0.2), otherwise it may be any radical, which is preferably inert, and advantageously an electron-withdrawing group (cf. preceding lines);

[0055] p is a positive integer, i.e. it cannot comprise the value 0.

[0056] EWG is advantageously fluorine, especially when p is less than or equal to 2.

[0057] The radicals X are advantageously all fluorine, especially when p is less than or equal to 2.

[0058] Another value of EWG (electron-withdrawing group) is when it equals chlorine; in this case, EWG is a chlorine.

[0059] p represents an integer advantageously not more than 4 and preferably not more than 2;

[0060] EWG advantageously represents an electron-withdrawing group whose optional functions are inert under the reaction conditions, advantageously fluorine or a perfluoro residue of formula $\text{C}_n\text{F}_{2n+1}$, with n being an integer not more than 8 and advantageously not more than 5.

[0061] The total carbon number of R_f is advantageously between 1 and 15 and preferably between 1 and 10.

[0062] It is advantageous that R_f should be of formula $\text{C}_r\text{F}_{2r+1}$ with r being an integer not more than 15 and advantageously between 1 and 10.

[0063] The present invention is particularly advantageous for radicals R_f of low molecular weight, i.e. those that are relatively volatile (with a boiling point at atmospheric pressure of not more than 100°C). The technique is particularly advantageous for radicals R_f containing a radical with an odd number of carbons, and particular mention should be made for radicals R_f of C_1 , C_2 and C_3 .

[0064] Radicals R_f higher than C_6 are less advantageous.

[0065] The compounds that give the most advantageous results are those in which Z is of structure Y—R_4 with Y being a chalcogen, preferably a light chalcogen, i.e. sulfur or oxygen and more particularly the latter.

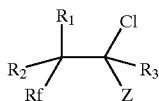
[0066] R_4 is a hydrocarbyl group, i.e. a group containing hydrogen and carbon. These hydrocarbyl groups may be alkyl (i.e. an alcohol residue of which the hydroxyl function is ignored), an aryl or an oxygenated acid residue (i.e. a residue whose acidic hydrogen is borne by an oxygen) from which an OH function has been removed. In this latter group, mention may be made of acyls, phosphoryls, phosphonyls, phosphinyls and sulfonyls. The acids $\text{R}_4\text{Y}(\text{O})_q$ advantageously have a pKa of not more than 10, preferably not more than 8 and more preferentially not more than 6. Acids with a Hammett constant that is greater than or equal to that of perfluoroalkane-sulfonic acids, and especially triflic acid, are not preferred.

[0067] The group R_4 is advantageously an electron-withdrawing group of the acyl type.

[0068] It is preferable for the molecule bearing the double bond not to contain a strongly reductive function, or a nucleophilic function capable of reacting with the sulfonyl chloride.

[0069] The total carbon number of the substrate of formula I is generally not more than 50 (one significant figure) and better still not more than 30. In particular, when R_f is of the type $\text{CX}_3(\text{CX}_2)_s$, the presence of halogens heavier than fluorine at the other end of the chain R_f liable to give spurious reactions, especially when the chain R_f is short (s less than or equal to 5 and, even, less than or equal to 4). As has been stated previously, another aim of the present invention is that of providing reaction intermediates that allow novel routes of access.

[0070] This aim is achieved by means of compounds corresponding to the formula:



[0071] with R_1 , R_2 , Z and R_f being chosen from the same values (and with the same preferences) as above, but with the following additional conditions:

[0072] with R_1 and R_2 chosen from hydrogen and hydrocarbyl radicals, with the condition that one of the radicals R_1 or R_2 at least is equal to H, and advantageously both of them;

[0073] with Z chosen from radicals of formula $(CHR')_m-Y-R_4$ in which R_4-Y is such that R_4YH is an oxygenated acid,

[0074] the possible aromatic nucleus (nuclei) being separated from said double bond by at least two atoms of sp^3 hybridization (in the case of Z , an oxygen atom and at least one carbon atom, advantageously at least two sp^3 carbon atoms; in the other cases, at least two sp^3 carbon atoms);

[0075] the total carbon number of the molecule being at least equal to $(6-m)$ and not more than 30, and advantageously in which:

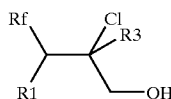
[0076] Y is a chalcogen, advantageously a light chalcogen, preferably oxygen;

[0077] R' represents a hydrocarbyl, advantageously of not more than four carbons, or preferably a hydrogen;

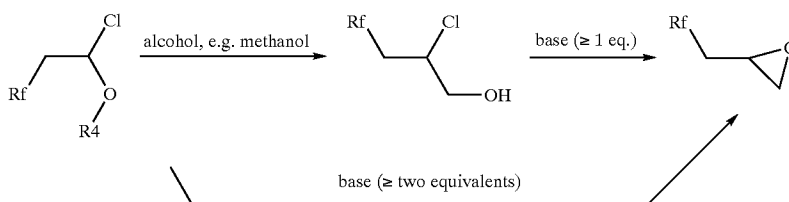
when R_3 is other than H, the compounds are highly reactive [lacuna] constitutes only reaction intermediates but remains identifiable, especially at low temperature by fluorine-19 NMR. When R_3 is hydrogen, these compounds are surprisingly stable. These two subfamilies decompose or are hydrolyzed to carbonyl, aldehyde or ketone derivatives, see the examples. This subfamily may thus be used to synthesize by hydrolysis, for example acid hydrolysis, aldehydes or ketones and derivatives thereof. A subsequent oxidation, which is known per se, of the aldehydes gives the corresponding acids.

[0083] Another advantageous subfamily lies in the alcohol and the corresponding esters in which m is equal to one and Y is oxygen and in which, advantageously, R_3 is H.

[0084] The alcohol is readily synthesized by alcoholysis of the corresponding ester, without touching the chlorine borne by the carbon atom adjacent to that bearing the ester function and then the alcohol:



[0085] The alcohol or ester readily lead, especially under the action of strong base (sodium hydroxide, potassium hydroxide or quaternary ammonium hydroxide), the associated acid of which has a pK_a at least equal to 12 and advantageously to 13, to epoxides:



[0078] m is equal to 1 or, preferably, to zero;

[0079] and R_4 is chosen from hydrocarbyl groups, advantageously from acyls.

[0080] It is advantageous for R_f to be of formula C_rF_{2r+1} with r being an integer not more than 15, advantageously between 1 and 10 and preferably not more than 4.

[0081] For steric reasons, it is preferable for said acid R_4-YH not to comprise any branching alpha or beta to the atom bearing the acidic proton, in general oxygen; thus, for example, in the case of a carboxylic acid, the atom bearing the carboxylic function, which is beta to the oxygen bearing the proton, is advantageously neither tertiary nor even secondary, nor does it correspond to the branching of an aromatic nucleus.

[0082] One subfamily of the above compounds is particularly novel, namely the family in which m is equal to zero;

[0086] See the examples below.

[0087] The epoxides $R_f-CHR_1CR'(O)CH_2$ are important organic intermediates given the importance of "perfluoro-alkylpropylene oxides and related compounds" in application on account of their common properties:

[0088] polymerization catalysts,

[0089] urethane-fluoropolyether acrylate copolymers,

[0090] treatment of metal surfaces,

[0091] transparent materials,

[0092] hydrophobic coatings,

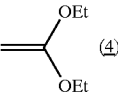
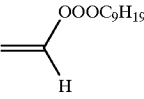
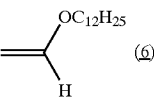
[0093] cosmetics.

[0094] As has been stated previously, for reasons of ease of synthesis according to the invention and for reasons of stability, it is desirable for Rf not to bear in the omega position (i.e. at the other end of the chain) of the longest chain, a halogen heavier than fluorine (i.e. chlorine, bromine or iodine).

[0095] The nonlimiting examples that follow illustrate the invention.

EXAMPLE 1 (COMPARATIVE)

[0096] Action of trifluoromethanesulfonyl chloride on enol ethers and esters in the presence of ruthenium activated with triphenylphosphine (for the operating conditions, see Kamigata et al., J. Chem. Soc. Perkin Trans., 1991, page 631, left-hand column).

Substrate	θ° C.	T(h)	DC % ^{(b)(1)}	DC % ^(a)	RY % ^(b)	Comments
 (4)	100° C.	24.5	100	nd ^(c)	0	- Formation with RY = 91.5% CF ₃ SO ₂ Et (characterization by ¹⁹ F NMR and GC/MS). - Detection by GC/MS of by products derived from (4): —CICH ₂ CH ₂ CO ₂ Et —CH ₃ CO ₂ Et
 (5)	100° C.	17.5	40	68	0	Detection by GC/MS analysis of many decomposition products of CH ₂ =CHOCOC ₉ H ₁₉ : E.g.: C ₉ H ₁₉ CO ₂ H
	120° C.	16	38	87.5	0	
 (6)	100° C.	16	49	100	0	Detection by GC/MS analysis of many decomposition products of CH ₂ =CHOC ₁₂ H ₂₅ : —C ₁₂ H ₂₅ OH (majority) —C ₁₁ H ₂₃ CHO —C ₁₁ H ₂₃ COCF ₃

^(a)GC assay with internal standard

^(b)¹⁹F NMR assay with internal standard

^(c)not determined

(&)

⁽¹⁾relative to the sulfonyl chloride

EXAMPLE 2

[0097] Action on Various Vinyl Ethers

[0098] The initiator (0.376 mmol), the alkene (9.4 mmol) then triflyl chloride (9.4 mmol) are successively introduced into a 60 mm Schott tube at 20° C. The reaction is that indicated in the general equation of the description with R₁, R₂, R₃=H.

Test (a)	Substrate R	Initiator	t(h)	Substrate	DC % ^(b)	RY % ^(b)
RON 240B	5 OCOC ₉ H ₁₉	(PhCO ₂) ₂	13.5	1/1	82	41
BJ 540A	OCOC ₉ H ₁₉	(PhCO ₂) ₂	7	1/1	77	45

-continued

Test (a)	Substrate R	Initiator	t(h)	Substrate	DC % ^(b)	RY % ^(b)
BJ 544B	OCOC ₉ H ₁₉	AIBN	17	1/1.2	76.5	50
BJ 545A	OCOC ₉ H ₁₉	AIBN	7	1/1.2	75.5	50
BOA 137	(12) OCOCH ₃	AIBN	7	1/1	82	52.5
BOA 9	(13) (CH ₂) ₇ CH ₃	AIBN	7	1/1.1	91	77.5

[0099] The addition products were identified by fluorine-19 NMR and by gas chromatography coupled to a mass spectrograph.

[0100] The reaction was performed at 90° C. and, at this temperature, the reaction is complete, or at the very least has ended, after 7 hours.

[0101] Contrary to the rutheniumtriphenylphosphine chloride system, free-radical initiators allow the addition of trifluoromethyl, on the one hand, and of chloride, on the other hand, to the double bond of enol esters.

EXAMPLE 3

[0102] Study of the Role of the Amount of Free-Radical Initiators

[0103] One equivalent of triflyl chloride, AIBN in variable proportions and 1.2 equivalents of vinyl laurate are successively introduced into a 60-ml Schott tube, the reaction mixture is then maintained at 90° C. for 7 hours while the solution is stirred on a heating block.

[0104] The crude reaction mixture is analyzed by gas chromatography and fluorine-19 NMR.

Mol % initiator	DC % ^(b)	DC % ^(c)	RY % ^(b)
0	70	57	25
1	77.2	—	43
4	84	86.5	56
6	85	95	54

EXAMPLE 4 (COMPARATIVE)

[0105] Influence of the Nature of the Triflyl Halide, Reaction with Perfluorobutanesulfonic Fluorides

[0106] Under conditions similar to the previous test, perfluorobutanesulfonic fluoride is tested in place of the triflyl chloride.

Substrate	R	DC % ^(b)	DC % ^(c)	RY % ^(b)
(12)	—OAc	27	79.5	0

[0107] Although the alkene reacts, the desired product is not obtained.

EXAMPLE 5 (COMPARATIVE)

[0108] In the Case of Styrene

[0109] The above operating conditions were repeated, using styrene as the vinyl substrate. The results are collated in the table below.

Test	DC % ^(a)	DC % ^(a)	Comments
BOA 1	65	10	By ¹⁹ F NMR and GC/MS the formation of the "dimer" is detected (2 diastereoisomers)

[0110] Oligomerization or polymerization products are mainly formed.

EXAMPLE 6

[0111] Comparison Between Vinyl Ethers and Vinyl Esters

[0112] The above operating conditions were carried out on various substrates using triflyl chloride. The substrates used have different values of Z.

Test	Z	DC % ^(a)	RY % ^(a)
BJ 542B	OC ₁₂ H ₂₅	68	23.5
BOA 142	SPh	91	22.5
BOA 137	OAc	82	52.5
RON 274	OCOC ₁₁ H ₂₃	85	54

EXAMPLE 7

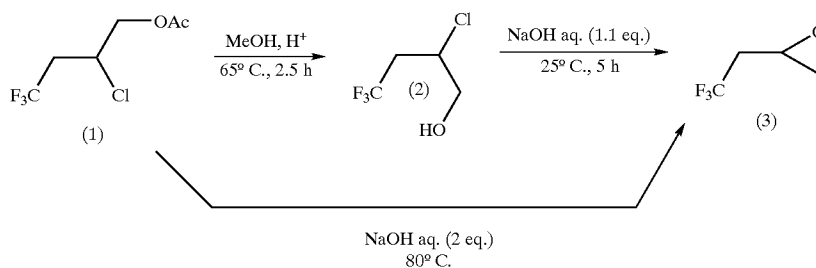
[0113] Unfavorable Role of the Phenyl Radical

[0114] The above conditions were used on various substrates, with the value of Z being varied. The results are collated in the table below. The ketone corresponds to the desired product after elimination of an acyl chloride.

Substrate	DC % ^(a)	RY % ^(a)	Formation of ketone
CH ₂ =CH—OAc	82	52.5	—
CH ₂ =C(CH ₃)—OAc	78.5	0	50
CH ₂ =C(Ph)—OAc	69	1.5	5
CH ₂ =C(CH ₃)—OSiMe ₃	89	0	28
CH ₂ =C(Ph)—OSiMe ₃	57.5	0	9

EXAMPLE 8

[0115] Experimental Section:



[0116] The acyl herein is such that Ac—O— is a propionate

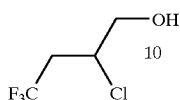
[0117] Synthesis Starting with 2-Chloro-4,4,4-trifluorobutyl Propionate (1)

[0118] 15% sodium hydroxide (107 mmol) and 2-chloro-4,4,4-trifluorobutyl propionate (1) (10.03 g, 49.0 mmol) are loaded into a perfectly stirred and standardized 100-ml reactor equipped with a condenser and a thermometer. The reactor is placed in an oil bath at 90° C. with stirring at 320 rpm. The temperature of the medium reaches 84° C. After 24 minutes, the system is cooled with a bath of cardice. The medium is two-phase and the lower phase is colorless. GC

allows the partial state of progress of the reaction to be monitored. The reactor is placed at 90° C. for 30 minutes at 520 rpm. The temperature of the medium reaches 84° C. The system is cooled in a bath of cardice. Monitoring by GC indicates the end of the reaction. The medium is two-phase and yellow. The lower phase is separated out by settling. 4.11 g (RY_{assayed}=46%) are recovered. In the same manner, a second batch is carried out (30 minutes with stirring at 520 rpm). 4.43 g (RY_{assayed}=43%) are recovered. The organic phases are distilled off under atmospheric pressure simply with a column head (t_{passage}=68-83° C.). 4.83 g of a colorless liquid are recovered (P_{mass}=96%).

[0119] Synthesis from the Alcohol (2):

[0120] 2-Chloro-4,4,4-trifluorobutan-1-ol (2)



(2)

[0121] 2-Chloro-4,4,4-trifluorobutyl propionate (1) (9.58 g, 95.8 mmol), methanol (92 ml, 2.3 mol) and concentrated sulfuric acid (0.53 g, 10 mmol) are loaded into a 250-ml three-necked flask equipped with a condenser, a thermometer, a septum and a magnetic stirrer. The reaction medium is heated to reflux (between 60 and 65° C.). The mixture is left stirring for 2.5 hours. Distillation is performed at atmospheric pressure to remove the methanol and the methyl acetate. The residue is distilled at reduced pressure (38 mmHg). The following are collected:

[0122] 1st between 38 and 58° C.: 0.318 g at more than 99% pure

[0123] 2nd between 60 and 66° C.: 10.15 g at more than 99% pure

[0124] 3rd between 57 and 35° C.: 0.63 g at more than 95% pure.

[0125] 11.1 g are thus finally collected. Assay by 19F NMR gives a RY_{isolated} (2)=69%.

[0126] b.p.=60-65° C./38 mmHg

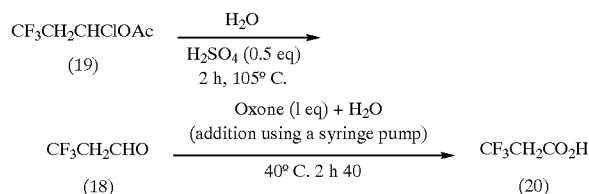
[0127] 4,4,4-Trifluoro-1,2-epoxybutane (3)

[0128] 15% sodium hydroxide (37 mmol) and 2-chloro-4,4,4-trifluorobutan-1-ol (2) are loaded into a perfectly stirred and standardized 100-ml reactor equipped with a condenser and a thermometer. The mixture is stirred at 20° C. for 1 hour 40 minutes at 250 rpm. A two-phase medium is obtained. GC of the mixture indicates a virtually complete DC. The mixture is allowed to settle for 2 hours. The two phases are separated. The organic phase is washed with 5 ml of H₂O. 3.1 g of crude product are recovered. ¹⁹F NMR analysis gives an RY_{assayed} (3)=68%

[0129] b.p.=68-69° C./627 mmHg

EXAMPLE 9

[0130]



[0131] 3,3,3-Trifluoropropanal (18)

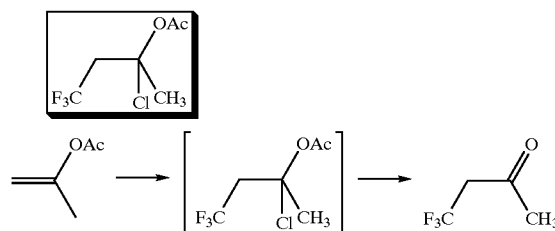
[0132] 1-Chloro-3,3,3-trifluoropropyl acetate (19) (10.02 g, 52.7 mmol), water (51 ml) and 95% sulfuric acid (1.5 ml, 26.6 mmol) are loaded into a 100-ml four-necked flask equipped with a magnetic stirrer, a cardice trap (connected to an antireturn bubbler) and a thermometer. The mixture is heated to 105° C. When the temperature of the medium reaches 87.5° C., a reflux appears. The temperature falls by a few degrees (83° C.). The mixture is heated for 2 hours. It is then cooled to ambient temperature and the trap is kept. The acetone in the trap is replaced with warm water. The trap is washed with water and the washing liquors are combined with the reaction medium. Assay by ¹⁹F NMR gives an RY_{assayed} (18) of 89%. The 3,3,3-trifluoropropanal (18) is stored in the acidic aqueous medium.

[0133] 3,3,3-Trifluoropropionic Acid (20)

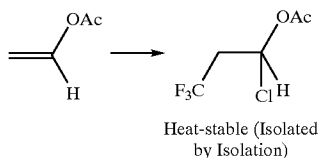
[0134] 1-Chloro-3,3,3-trifluoropropyl acetate (19) (1.0 g, 5.3 mmol), water (5 ml) and 95% sulfuric acid (0.15 ml, 2.6 mmol) are loaded into a 50-ml three-necked flask equipped with a magnetic stirrer, a cardice trap (connected to an antireturn bubbler), a thermometer and a Teflon tube. The mixture is heated to 105° C. When the temperature of the medium reaches 92° C., a reflux appears. The temperature falls by a few degrees (87° C.). The mixture is heated for 2 hours. It is then allowed to cool to ambient temperature, and the trap is kept. The acetone in the trap is replaced with warm water. The trap is washed with a minimum amount of water. Assay by ¹⁹F NMR gives an RY_{assayed} (20) of 73% (3.88 mmol). The solution of Oxone® (2.25 g, 3.67 mmol) in 10 ml of water is prepared. This solution is added by syringe pump over 30 minutes at 40° C. The mixture is left at 40° C. for 2 hours 15 minutes. 2.07 mmol of acid are obtained with an RY_{oxidation} (20)=73%.

EXAMPLE 10

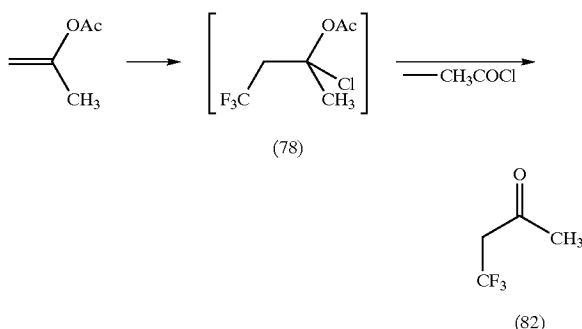
[0135]



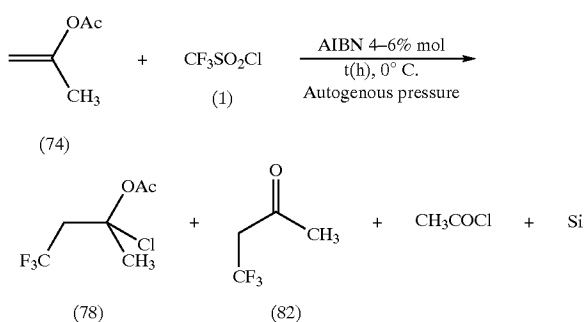
[0136] relative to:



[0137] The presence of a CH₃ unit is not an inconvenience for the trifluoromethylation reaction. However, the product of vicinal-chlorotrifluoromethylation is not isolated; as a result of the fact that there is now a tertiary carbon instead of a secondary carbon—as in CF₃CH₂CHClOAc—this reaction brings about a predominant elimination of acetyl chloride:



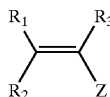
[0138] As shown by the results below, the intermediate (78) was detected by working at lower temperature and by analyzing the reaction medium after reaction for 1 to 3 hours:



Test	(1)/ (74)	t θ° C.	t (h)	DC % (1) % ^(b)	DC % (74) % ^(a)	RY (78) % ^(b)	RY (82) % ^(b)
BJ665	1/1	80	1	60	65	28.5	7.5
			2	68	75.5	21	19
BJ666	1/1	90	1	69	78	20	23
			2	72	90	5	39
			3	76	>95	1	39.5

[0139] (a) GC assay with internal standard, (b) assay by ¹⁹F NMR with internal standard: (78): δ=7.84 ppm (/TFA) and (82): δ=8.97 ppm (/TFA).

1. A process for functionalizing a double bond corresponding to formula I:



in which R₁, R₂ and R₃, which may be identical or different, are chosen from hydrogen and hydrocarbyls attached to said double bond via an sp³ carbon;

in which z is chosen from:

halogens, advantageously chlorine and fluorine;

residues such that ZH is an oxygenated acid;

radicals of formula (CHR')_m-Ξ with Ξ chosen from halogens;

and radicals of formula (CHR')_m-Y(O)_q-R₄ in which

Y is a chalcogen, advantageously a light chalcogen;

q is zero or an integer not more than 3, advantageously not more than 2 and preferably not more than 1, with the condition that when Y is oxygen, q is equal to zero;

R' represents a hydrocarbyl, advantageously of not more than four carbons, or preferably a hydrogen;

m is equal to 1 or preferably to zero;

and R₄ is chosen from a hydrocarbyl or silyl group;

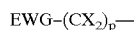
by the action of sulfonyl chloride perhalogenated on the sulfur-bearing carbon (of the sulfonyl function) in the presence of a free-radical initiator, preferably by homolytic cleavage.

2. The process as claimed in claim 1, characterized in that Z is of the nature Y—R₄ with Y being a light chalcogen.

3. The process as claimed in claims 1 and 2, characterized in that R₄ is an electron-withdrawing group.

4. The process as claimed in claims 1 to 3, characterized in that the free-radical initiator is an initiator by homolytic cleavage.

5. A process as claimed in claims 1 to 4, characterized in that the perhalogenated sulfonyl chloride corresponds to the formula R_f-SO₂-Cl in which R_f corresponds to the formula:



in which the radicals X, which may be similar or different, represent a chlorine, a fluorine or a radical of formula C_nF_{2n+1} with n being an integer not more than 5 and preferably not more than 2, with the condition that at least one of the radicals X is fluorine;

in which p represents an integer not more than 2;

in which EWG represents an electron-withdrawing group, the possible functions of which are inert under the reaction conditions, advantageously fluorine or a perfluoro residue of formula C_nF_{2n+1}, with n being an

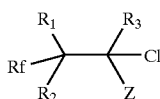
integer not more than 8 and advantageously not more than 5, the total number of carbon in R_f advantageously being between 1 and 15 and preferably between 1 and 10.

6. The process as claimed in claims 1 to 5, characterized in that R_f contains not more than 6 carbon atoms, advantageously not more than 5 and preferably not more than 3.

7. The process as claimed in claims 1 to 6, characterized in that Y is oxygen.

8. The process as claimed in claims 1 to 7, characterized in that R_4 is an acyl of not more than 15 carbon atoms and preferably not more than 10 carbon atoms.

9. A compound of formula (II):



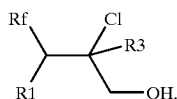
with R_1 , R_2 , Z and Rf being chosen from the same values (and with the same preferences) as above, but with the following additional conditions:

with R_1 and R_2 chosen from hydrogen and hydrocarbyl radicals, with the condition that one of the radicals R_1 or R_2 at least is equal to H, and advantageously both of them;

with Z chosen from radicals of formula $(CHR^*)_m-Y-R_4$ in which R_4Y is such that R_4YH is an oxygenated acid, the possible aromatic nucleus (nuclei) being separated from said double bond by at least two atoms of sp^3 hybridization (in the case of Z, an oxygen atom and at least one carbon atom, advantageously at least two sp^3 carbon atoms; in the other cases, at least two sp^3 carbon atoms);

the total carbon number of the molecule being at least equal to $(6-m)$ and not more than 30. Use of a compound of formula (II) in which m is equal to 1, to prepare a 3-perfluoroalkyl-1,2-epoxypropane:

10. A compound of formula (III)



11. The use of compounds of formula (III) to prepare a 3-perfluoroalkyl-1,2-epoxypropane.

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