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(56) Documents Cited:
US 4798680 A
Israel Journal of Chemistry, vol. 17, no. 1-2, 1978, pages 148-149
JP H02235828
JP H02167240
JP H02191233
JP H09110980

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Other: WPI, EPODOC, CAS ONLINE

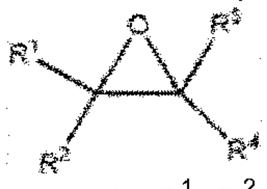
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(54) Title of the Invention: **Methods**
Abstract Title: **A method for preparing a partially fluorinated alcohol**

(57) A method for preparing a partially fluorinated alcohol, comprises reacting an epoxide:



wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising hydrogen, fluorine, chlorine, bromine, iodine, CF_3, alkyl, fluoroalkyl, haloalkyl with a fluorinating agent is provided. The fluorinating agent may be HF or a complex of HF with a nitrogen containing species, such as Olah's reagent (HF: Pyridine complex). A method for preparing a partially fluorinated carbonate ester comprising reacting a fluorohydrin and COX_2 wherein X is selected from the group comprising -F, -Cl, -CH_3, CCl_3, diimidazole and disuccinimidyl is described. The use of a fluorinated carbonate ester or composition comprising a fluorinated carbonate ester as a solvent, preferably in battery applications is described. A method of preparing a fluorinated compound by reaction a fluorohydrin with a fluorinating agent is described. A method of preparing a partially fluorinated epoxide by reacting a partially fluorinated alkene with an oxidising agent is described.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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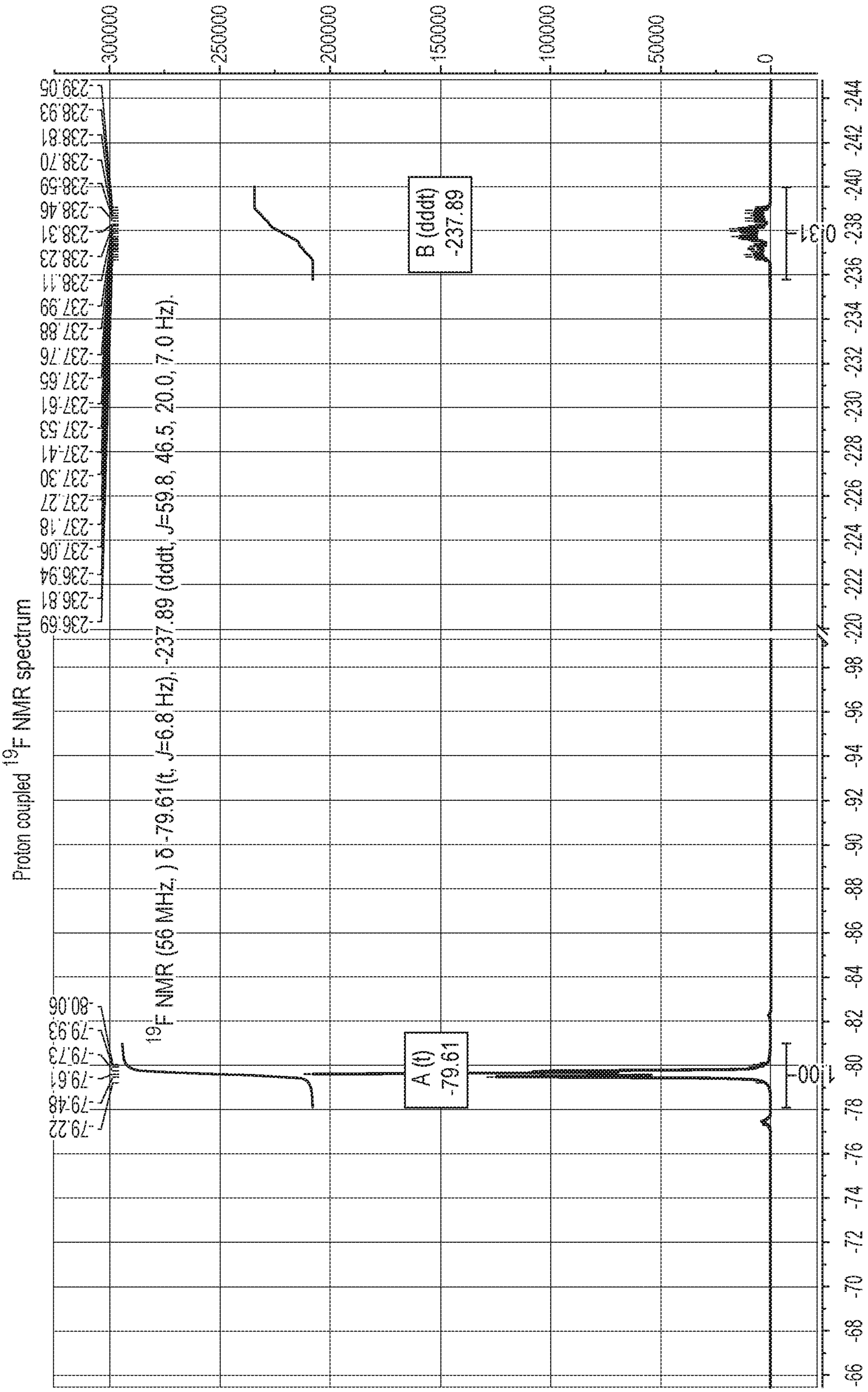


FIG. 1

Methods

The present invention relates to methods of preparing partially fluorinated alcohols (fluorohydrins) from fluorinated epoxides and preparing fluorinated carbonate esters from fluorohydrins.

Fluorohydrins are useful as solvents and as synthetic building blocks from which various species such as esters, ethers, ketones, aldehydes and acids can be prepared. Of particular interest is their utility in the preparation of fluorinated carbonate esters, which are an important class of materials with significant commercial value. Fluorinated carbonate esters are commonly used without modification as synthetic intermediates and as solvents in electronic devices such as batteries (e.g. lithium ion batteries) and to manufacture products such as lubricants, sealants, and coatings.

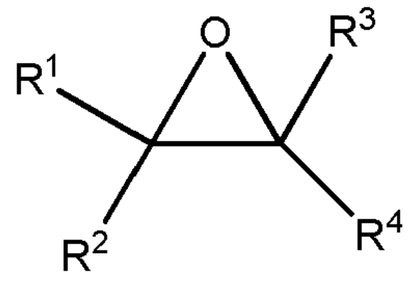
The production of fluorohydrins from epoxides is known in the art. For example, Olah described a general method for preparing fluorohydrins by ring opening epoxides with a nucleophilic source of fluoride (G. A. Olah et al, Israel Jr. Chem., 17(1978),148-149). However, Olah did not extend this work to the preparation of fluorohydrins from fluorinated epoxides.

The ring opening of the fluorinated epoxide, 2,3-epoxy1,1,1-trifluoropropane (TFPO), with various nucleophiles to form fluorohydrins was generally described in a review of the chemistry of TFPO by Uneyama in Jr. Fluorine Chem., 105(2000) 285-293. However, this review was silent on the possibility or likely outcome of attempting to ring open TFPO or indeed any other fluorinated epoxide with nucleophilic fluorinating agents as taught by Olah.

General methods for the production of carbonate esters from alcohols and a carboxylating agent are known in the art, see for example “March’s Advanced Organic Chemistry”, M. B. Smith and J. March, 6th edition, page 1276. However, the production of fluorinated carbonate esters from fluorohydrins and carboxylating agents is unknown as are the products of such reactions.

METHODS OF THE INVENTION

According to a first aspect of the invention there is provided a method for preparing a partially fluorinated alcohol, comprising reacting a fluorinated epoxide:

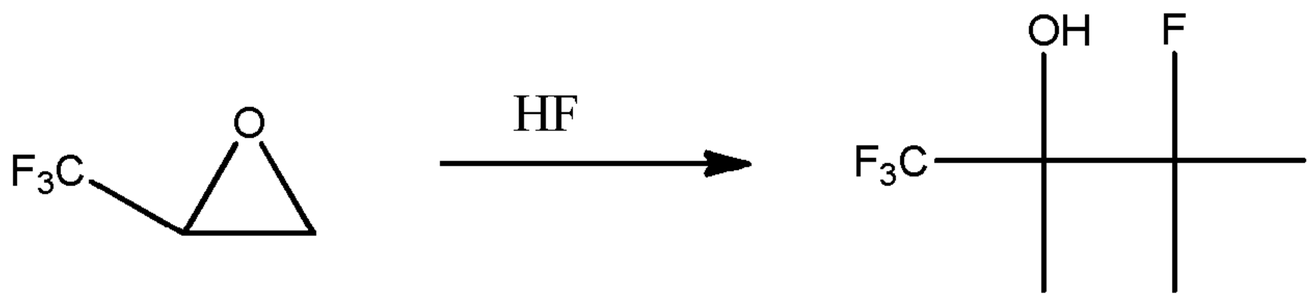


wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with a fluorinating agent.

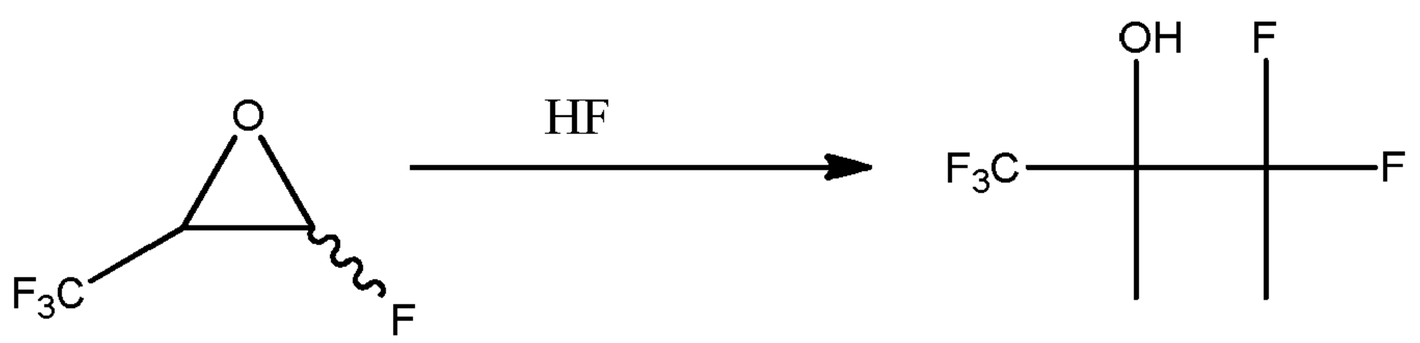
Preferably at least one of R^1 to R^4 comprises F, CF_3 or fluoroalkyl.

Preferably the fluorinating agent comprises a nucleophilic fluorinating agent. Preferred examples of fluorinating agents include HF and complexes of HF with nitrogen containing species, such as Olah's reagent (HF:Pyridine complex), with urea, or with a tertiary amine.

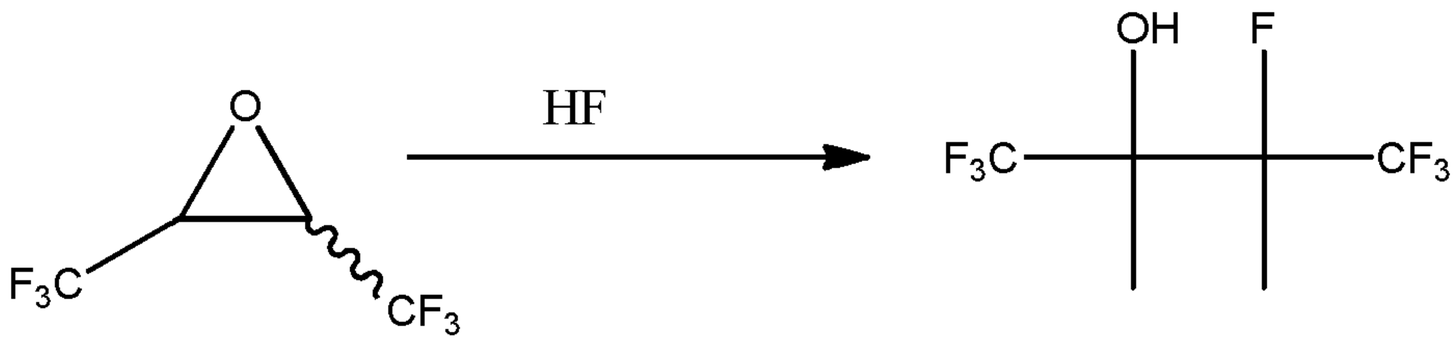
The method may comprise reacting an epoxide of 3,3,3-Trifluoropropene (1243zf) with HF and/or Olah's reagent to form $CF_3CH(OH)CH_2F$.



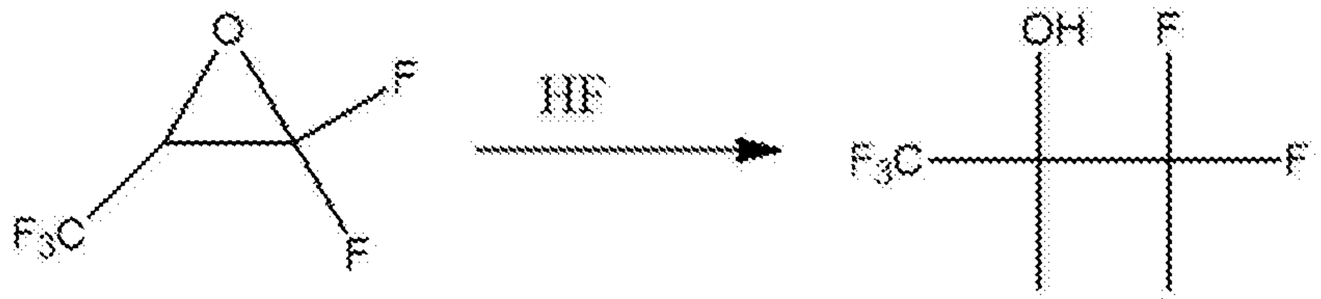
The method may comprise reacting an epoxide of 1,3,3,3-Tetrafluoropropene (1234ze) with HF and/or Olah's reagent to form $CF_3CH(OH)CHF_2$.



The method may comprise reacting an epoxide of 1,1,1,4,4,4-hexafluoro-2-butene (1336mzz) with HF and/or Olah's reagent to form $CF_3CH(OH)CHF(CF_3)$.

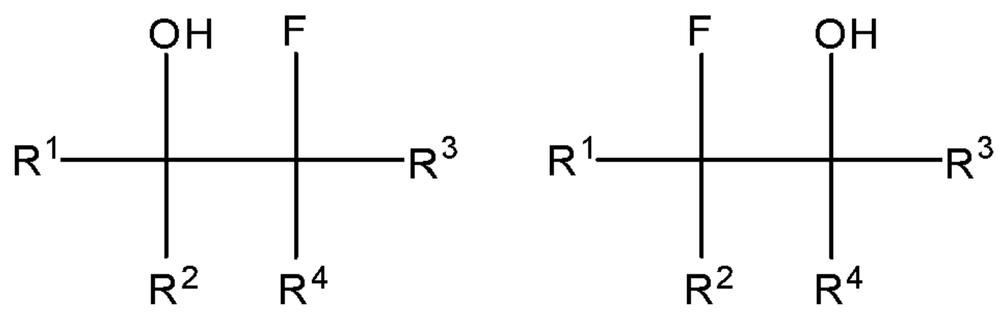


The method may comprise reacting an epoxide of 1,1,3,3,3-Pentafluoropropene (1225zc) with HF and/or Olah's reagent to form $CF_3CH(OH)CF_3$.



COMPOUNDS & COMPOSITIONS OF THE INVENTION

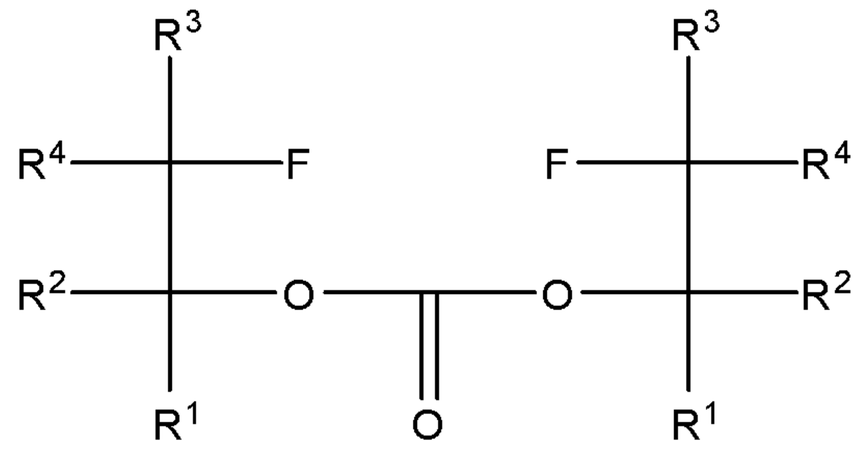
According to a second aspect of the invention there is provided compounds with the structure



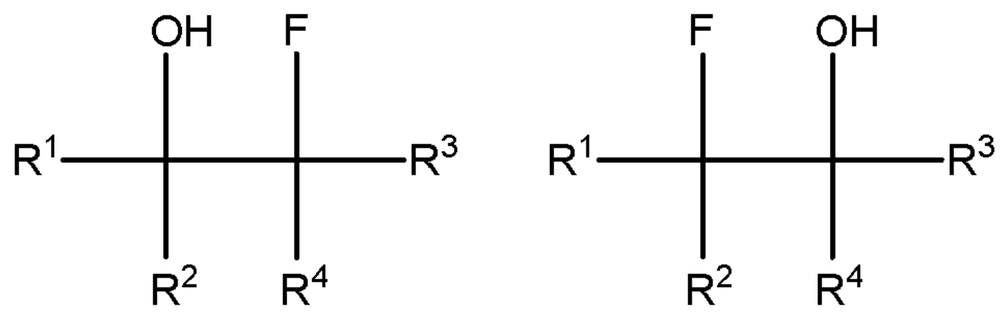
wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl, with the provision that the compound is not 1,1,1,3-tetrafluoropropan-2-ol.

The compounds of the second aspect of the invention may be used in the preparation of a carbonate ester.

According to a third aspect of the invention there is provided a method for preparing a partially fluorinated carbonate ester with the structure



comprising reacting a fluorohydrin

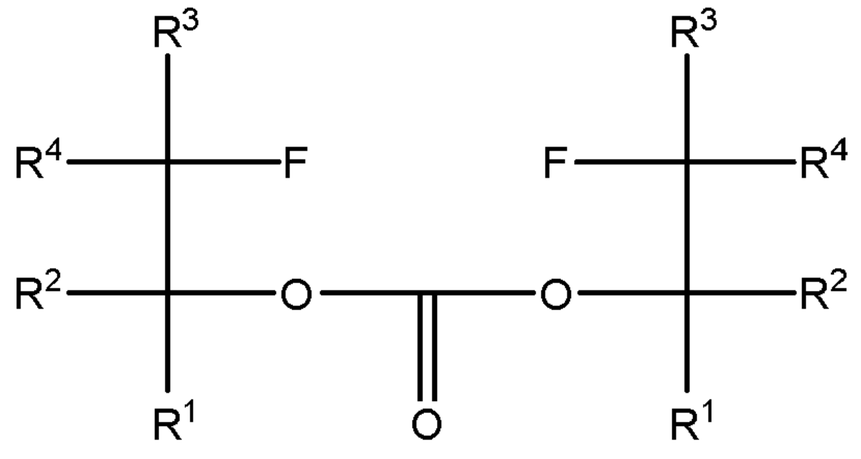


wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with COX_2, wherein X is selected from the group comprising -F, -Cl, $-CH_3$, CCl_3, diimidazole, disuccinimidyl.

Preferably 2 equivalents (on a molar basis) of the fluorohydrin are used per 1 equivalent of COX_2.

Alternatively, 1 equivalent of the fluorohydrins of this invention maybe used with 1 equivalent of an alcohol species (a branched or linear monohydric/polyhydric alcohol) to prepare asymmetric carbonate esters.

The compounds produced in a method according to the third aspect of the invention are covered by the fourth aspect of the invention. According to the fourth aspect of the invention there is provided a compound with the structure



wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl.

The compounds of the fourth aspect of the invention may be also used as a battery solvent component (e.g. in a lithium ion battery). Here the compounds are found to be beneficial as a result of their physical properties, electrochemical stability, compatibility with battery components such as battery electrodes (cathodes and anodes) including electrodes comprising carbon and silicon, lithium containing electrolyte salts, separators, binders, current collectors and low flammability.

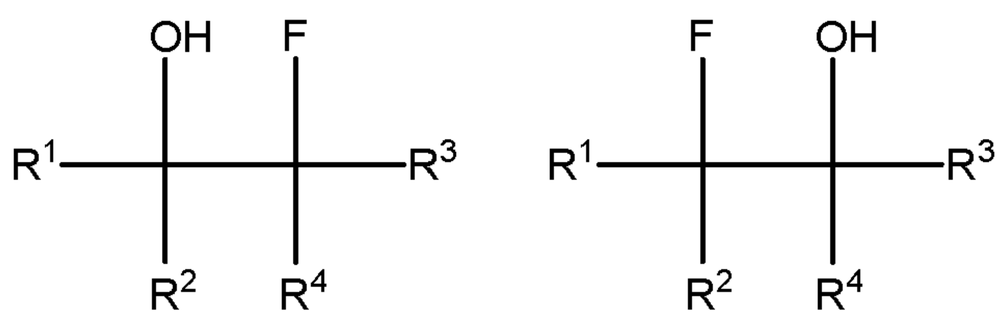
The compounds of the fourth aspect of the invention may also be used with other solvents and additives such as other linear and cyclic carbonate esters.

Preferably when used as a solvent the composition comprises an electrolyte salt. Preferred examples of electrolyte salts include lithium-based electrolytes such as those selected from the group comprising lithium hexafluorophosphate ($LiPF_6$), lithium triflate ($LiSO_3CF_3$), lithium bis(fluorosulfonyl)imide ($Li(FSO_2)_2N$) and lithium bis(trifluoromethanesulfonyl)imide ($Li(CF_3SO_2)_2N$).

The compounds of the second aspect of the invention may be used in the preparation of a (more highly) fluorinated derivative. One or more of the R groups may be substituted by fluorine. In the process the R groups to be altered by fluorination are preferably selected from the group comprising H, Cl, Br, I.

Depending on the nature of the R group(s) being modified the preparation process for the fluorinated derivative may comprise a multi-stage process; preferably a two-stage process. In a preferred two stage process a first stage is the modification of the targeted R group(s) to a (different) halogen group, preferably to a chlorine group (with a suitable chlorinating agent such as chlorine); in a second stage the chlorine group is modified to a fluorine group (with a suitable fluorinating agent such as HF or a metal fluorine salt, such as NaF, KF). It will be appreciated that where the R group(s) targeted already comprises a halogen, other than fluorine, a two-stage process with substitution of the halogen with chlorine may not be necessary.

Thus compounds

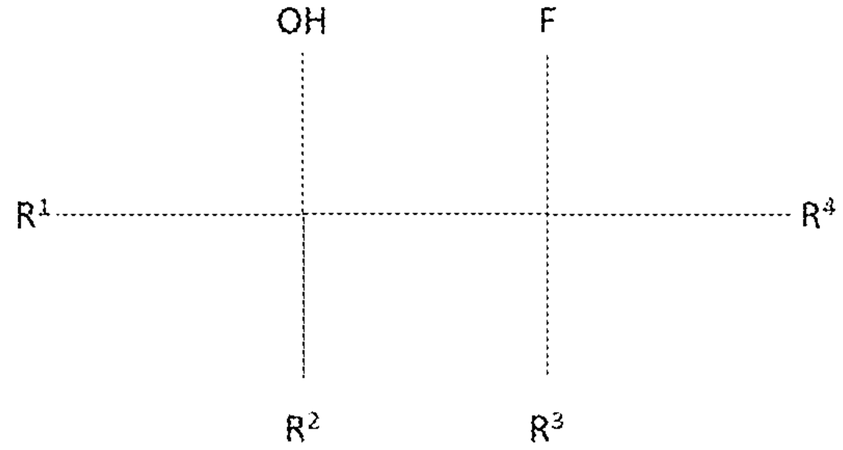


wherein at least 2 of R^1 to R^4 independently comprises H, Cl, Br, I may be converted to (more highly) fluorinated derivatives.

In the fluorinated derivatives preferably at least 2 and more preferably at least 3 of R^1 to R^4 independently comprises F, CF_3 or a fluoroalkyl. Preferably at least 1 of R^1 to R^4, and more preferably 1 of R^1 to R^4 independently comprises H. Most preferably 1 of R^1 to R^4 comprises

CF_3, two of R^1 to R^4 comprise F and one of R^1 to R^4 comprises H. Most preferably the fluorinated derivative comprises hexfluroroisopropanol.

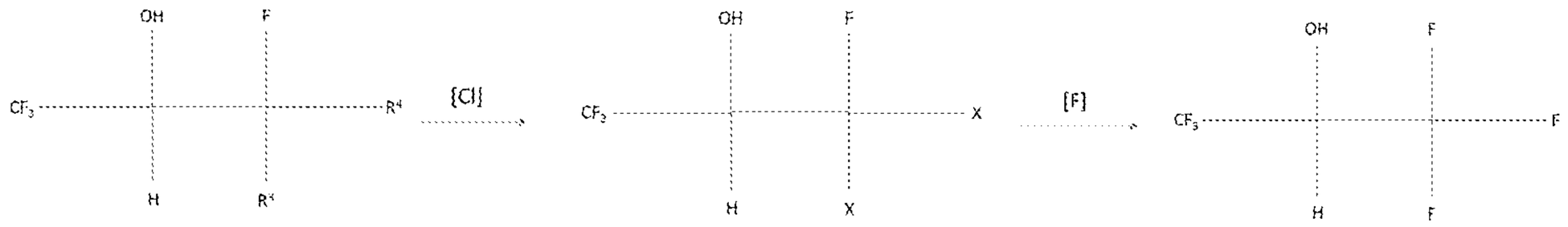
A preferred reaction pathway occurs for the compound



wherein in the preferred alternatives

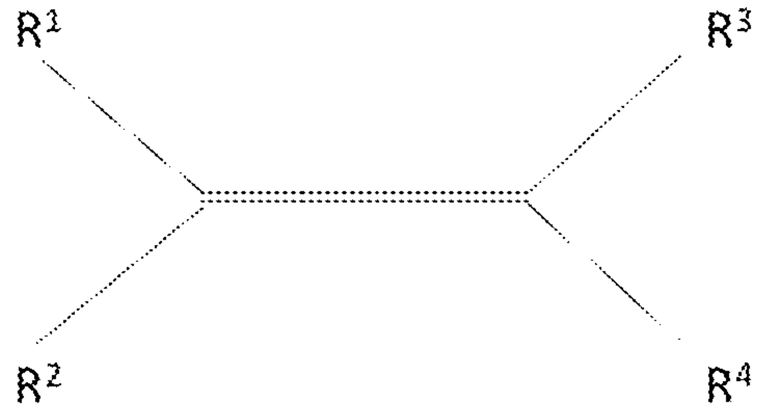
- R^1 is $-CF_3$, R^2 is H and both R^3 and R^4 are H.
- R^1 is $-CF_3$, R^2 is H; one of R^3 and R^4 is H, one of R^3 and R^4 is F.

This preferred pathway is shown below.



X is either F or Cl.

The epoxides useful in the first aspect of the invention may prepared from a fluorinated alkene. According to a fifth aspect of the invention there is provided a method for preparing a partially fluorinated epoxide, comprising reacting a fluorinated alkene:



wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with an oxidising agent.

Preferably at least one of R^1 to R^4 comprises F, CF_3 or fluoroalkyl.

Preferred examples of oxidising agent include air, oxygen and oxygen containing compounds such as peroxides, per-salts and compounds of oxygen with other elements such as hypohalites. Preferably the oxidising agent comprises a hypohalite such as chlorite.

Preferably, the compound reacted with the oxidising agent is a tetrafluoropropene. Most preferably, one of R^1 and R^2 is $-CF_3$ and one of R^3 and R^4 is -F. Thus, the tetrafluoropropene is 1,3,3,3-Tetrafluoropropene (1234 ze) or 2,3,3,3-Tetrafluoropropene (1234yf).

According to a sixth aspect of the invention there is provided a method for preparing a fluorohydrin comprising the fifth and the first aspects of the invention.

The invention will now be illustrated with reference to the following non-limiting examples.

Examples

Example 1 – Ring opening of an epoxide with Olah's reagent

The following steps were followed.

- The reactor was charged with Olah's reagent (70 % HF:Pyridine, 5 ml) and cooled in an ice batch with stirring.
- 2,3-epoxy1,1,1-trifluoropropane (TFPO) (3.4 g) was then added dropwise.
- At the end of the addition the reaction mixture was allowed to warm up to room temperature; stirring was continued for 48 hours.
- After 48 hours the reaction mixture was quenched with ice.
- Salt was added, and the product extracted with diethyl ether (3 x 5 ml). The diethyl ether extracts were combined, washed with saturated potassium bicarbonate solution and water before being dried over anhydrous sodium sulphate. Diethyl ether was removed in vacuo to yield the desired product as a clear, colourless liquid boiling point 91-93^{o}C. The identity of this product was confirmed by NMR spectroscopy.

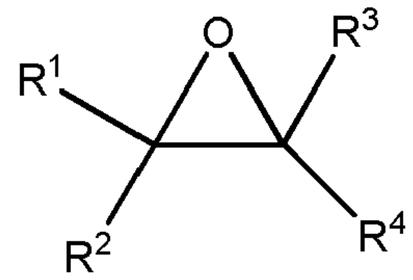
Figures

The Figures illustrates the results of various spectroscopic analytical techniques carried out on some of the reaction products from the Examples.

Figure 1 shows a ^{19}F NMR spectrum of the reaction product of 2,3-epoxy1,1,1-trifluoropropane (TFPO) with Olah's reagent.

Claims

1. A method for preparing a partially fluorinated alcohol, comprising reacting an epoxide:



wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with a fluorinating agent.

2. A method according to claim 1, where the fluorinating agent comprises a nucleophilic fluorinating agent.

3. A method according to claim 1 or 2, where the fluorinating agent is selected from HF and complexes of HF with nitrogen containing species, such as Olah's reagent (HF:Pyridine complex), with urea, or with a tertiary amine.

4. A method according to claim 3, where the ratio of HF to pyridine is 7:3 by weight.

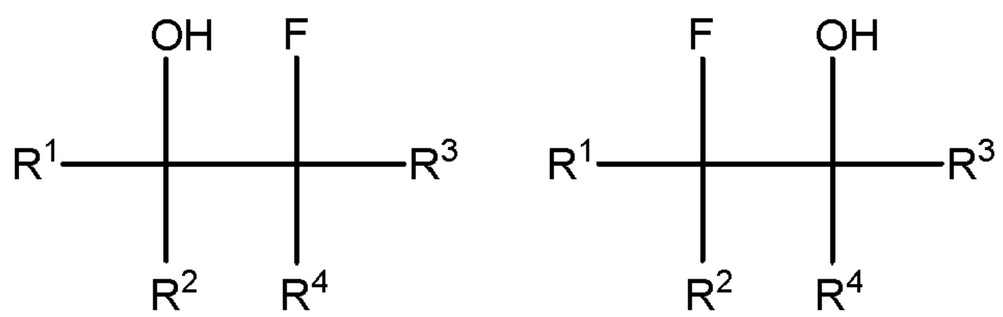
5 . A method according to any one of claims 1 to 4, where R^1 is -F and R^3 is $-CF_3$; R^2 and R^4 are -H.

6. A method according to any one of claims 1 to 4, where R^1 is $-CF_3$ and R^3 is $-CF_3$; R^2 is -H and R^4 are -H.

7. A method according to any one of claims 1 to 4, where R^1 is $-CF_3$, R^2, R^3 and R^4 are -H.

8. A method according to any one of claims 1 to 4, where R^1 is $-CF_3$, R^2,is -H R^3 and R^4 are -F.

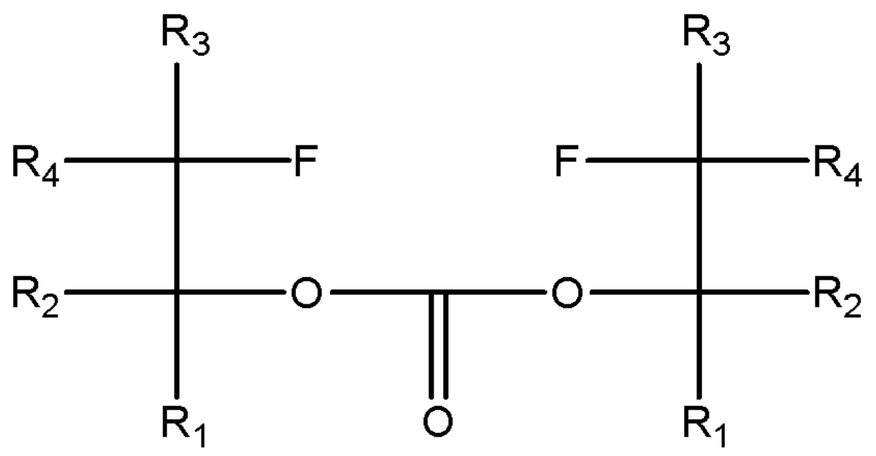
9. Compounds with the structure



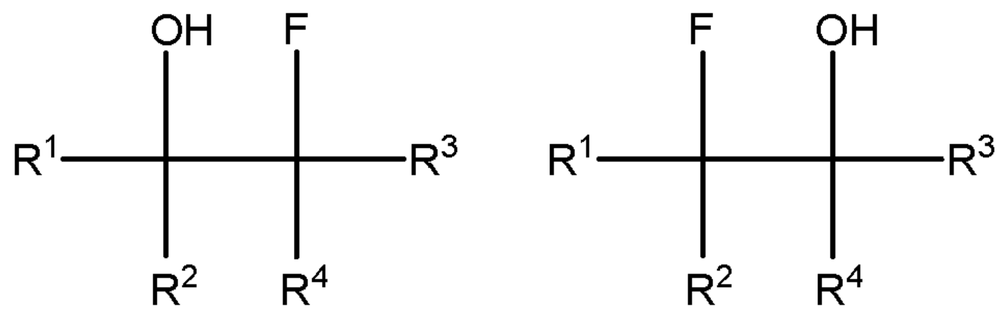
wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl, with the provision that the compound is not 1,1,1,3-tetrafluoropropan-2-ol.

10. A compound of claim 9, formed by the process of one of claims 1 to 8.

11. A method for preparing a partially fluorinated carbonate ester with the structure

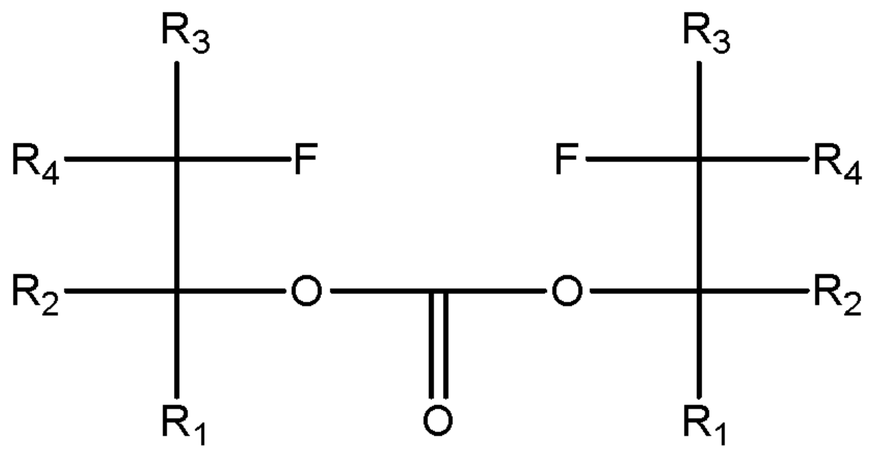


comprising reacting a fluorohydrin with the structure

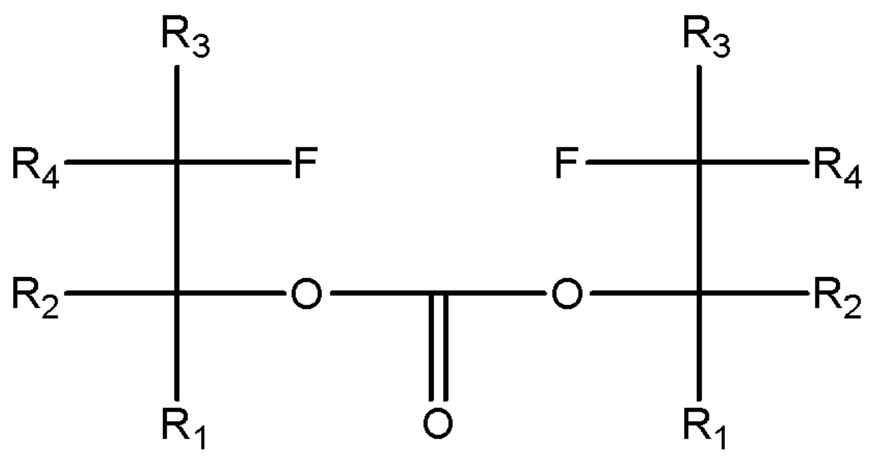


wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with COX_2, wherein X is selected from the group comprising -F, -Cl, $-CH_3$, CCl_3, diimidazole, disuccinimidyl.

12. A compound with the structure



13. A composition comprising a compound with the structure

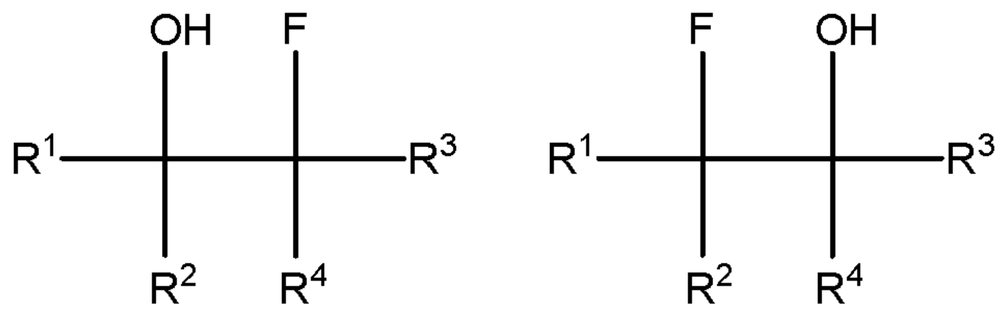


14. The use of a compound according to claim 12 or a composition according to claim 13 as a solvent, for example, in battery applications.

15. A solvent composition comprising a compound according to claim 12 or a composition according to claim 13.

16. A solvent composition according to claim 15, wherein the composition comprises an electrolyte comprising a lithium salt, selected from the group comprising lithium hexafluorophosphate ($LiPF_6$), lithium triflate ($LiSO_3CF_3$), lithium bis(fluorosulfonyl)imide ($Li(FSO_2)_2N$) and lithium bis(trifluoromethanesulfonyl)imide ($Li(CF_3SO_2)_2N$)..

17. A method for preparing a fluorinated compound, comprising reacting a compound:



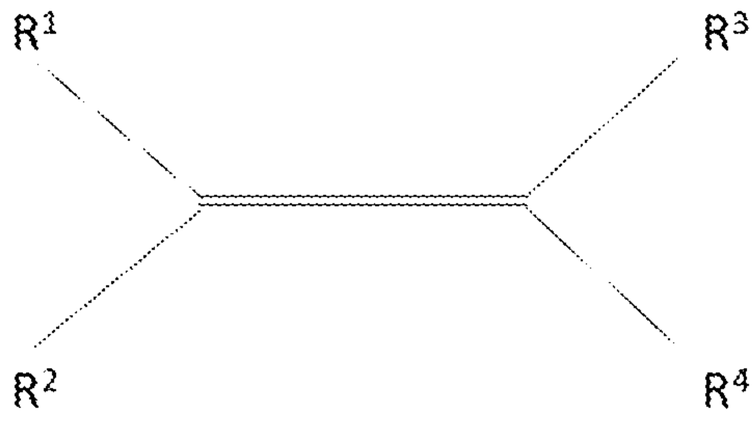
wherein at least 2 of R^1 to R^4 independently comprise H, Cl, Br, I with a fluorinating agent

18. A method according to claim 17, wherein in the fluorinated compound at least 2 of R^1 to R^4 independently comprise F, CF_3 or a fluoroalkyl.

19. A method according to claim 17 or 18, wherein in the fluorinated compound at least 1 of R^1 to R^4 comprises H.

20. A method according to claim 17, 18 or 19, wherein the fluorinated compound comprises hexfluroroisopropanol.

21. A method for preparing a partially fluorinated epoxide, comprising reacting a partially fluorinated alkene:



wherein R^1, R^2, R^3 and R^4 are independently selected from the group comprising H, F, Cl, Br, I, CF_3, alkyl, fluoroalkyl, haloalkyl with an oxidising agent.

22. A method according to claim 21, wherein the oxidising agent is selected from the group comprising air, oxygen and oxygen containing compounds such as peroxides, per-salts and compounds of oxygen with other elements such as hypohalites.

23. A method according to claim 21 or 22, wherein the oxidising agent comprises a hypohalite such as chlorite.

23. A method according to claim 20, 21 or 22, wherein the alkene comprises a tetrafluoropropene, such as 1,3,3,3-Tetrafluoropropene (1234ze) or 2,3,3,3-Tetrafluoropropene (1234yf); or a pentafluoropropene, such as 1,1,3,3,3-Pentafluoropropene (1225zc).

24. A method for preparing a partially fluorinated alcohol, comprising a method for preparing a partially fluorinated epoxide according to any one of claims 20 to 23 and a method comprising reacting an epoxide according to any one of claims 1 to 7.

25. A method for preparing a partially fluorinated alcohol, comprising a method for preparing a partially fluorinated epoxide according to any one of claims 20 to 23, a method comprising reacting an epoxide according to any one of claims 1 to 7, and a method for preparing a fluorinated compound according to any one of claims 16 to 19.

Intellectual Property Office

Application No:	GB1903909.8	**Examiner:**	Dr Alistair Longshaw
Claims searched:	1 - 8	**Date of search:**	27 August 2019

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1 - 4	Israel Journal of Chemistry, vol. 17, no. 1-2, 1978, pages 148-149 Olah and Meidar, "Synthetic Methods and Reactions. 43. Preparation of Fluorohydrins from Epoxides with Pyridinium Poly-hydrogen Fluoride" - See whole document, especially table 1 and experimental
X	1 - 4	US 4798680 A (NOHIRA et al.) - See whole document, especially example 1
X	1 - 4	JP H02235828 A (NIPPON MINING CO) - See WPI Abstract Accession No. 1990-326090 and formula (1) and (II)
X	1 - 4	JP H02167240 A (NIPPON MINING CO) - See WPI Abstract Accession No. 1990-242001 and formula (I)
X	1 - 4	JP H02191233 A (NIPPON MINING CO) - See WPI Abstract Accession No. 1990-271376 and formula (1)
X	1, 2 and 7	JP H09110980 A (JAPAN ENERGY CORP) - See WPI Abstract Accession No. 1997-295035

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

C07B; C07C; C07D

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, CAS ONLINE

Intellectual Property Office

International Classification:

Subclass	Subgroup	Valid From
C07C	0029/62	01/01/2006
C07B	0039/00	01/01/2006
C07C	0031/38	01/01/2006
C07D	0303/08	01/01/2006