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CA 2527802 A1 2007/06/12

(21) 2 527 802

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2005/12/12

(41) Mise à la disp. pub./Open to Public Insp.: 2007/06/12

(51) Cl.Int./Int.Cl. *C01D 15/00* (2006.01), *C01D 15/04* (2006.01), *C07F 1/02* (2006.01)

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(54) Titre : SYNTHESE DE SELS DE LITHIUM D'IMIDES ANHYDRES CONTENANT UN SUBSTITUANT FLUOROSULFONYLE OU FLUOROPHOSPHORYLE

(54) Title: SYNTHESIS OF ANHYDROUS IMIDES LITHIUM SALTS CONTAINING FLUOROSULFONYL OR FLUOROPHOSPHORYL SUBSTITUENT

(57) Abrégé/Abstract:
The invention relates to a process for the industrial synthesis of acid imides salts and their anhydrous lithium imides salts, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical, such as $(FSO_2)_2NLi$ or $(F_2PO)_2NLi$.

Abstract:

The invention relates to a process for the industrial synthesis of acid imides salts and their anhydrous lithium imides salts, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical, such as $(FSO_2)_2NLi$ or $(F_2PO)_2NLi$.

1. Field of the invention:

The invention relates to a process for the industrial synthesis of anhydrous lithium imides salts, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical, such as $(FSO_2)_2NLi$ or $(F_2PO)_2NLi$.

2. Description of the prior art:

Salts of low basicity anions are widely used in various industrial fields such as polymerization process, catalysis or batteries. In this last huge market application, lithium salt are one of the key component for electrolytes preparation. Numerous lithium salts have been or are used in lithium batteries such as CF_3SO_3Li, $LiBF_4$, $LiPF_6$ or $LiN(SO_2CF_3)_2$. In addition to provide stable and conductive electrolytes when mixed with suitable organic solvents, lithium salts for batteries applications need to be obtain in an anhydrous state (typically with water content inferior to 1000 ppm and preferably inferior to 100 ppm).

$LiPF_6$ is the main salt used in commercial lithium-ion ("Li-Ion") technology but it presents some drawbacks, especially a limited thermal stability which lowered the security of the battery and a poor stability to hydrolysis. On the other hand, salt such as $LiN(SO_2CF_3)_2$ are stable up to 300°C and are not sensitive to hydrolysis but, due to cathodic corrosion of aluminum current collector, this salt is only used as an additive in Li-Ion technology.

A valuable compromise has been found by replacing CF_3- radicals by fluorine atoms in $LiN(SO_2CF_3)_2$. Indeed, $LiN(SO_2F)_2$ imide is in particular more conductive and more stable on storage than $LiPF_6$. Thus $LiN(SO_2F)_2$ ("LiFSI") is a valuable substitute of at least $LiPF_6$.

A few preparation process of LiFSI or its acid form are described. For example, concerning preparation of the acid,

bis(fluorosulfonyl)imide $(FSO_2)_2NH$ ("HFSI") is prepared by action of fluorosulfonic acid FSO_3H with urea $H_2NC(O)NH_2$. Pure acid is then obtained by NaCl treatment of bulk media in dichloromethane followed by a distillation [Appel & Eisenhauer, Chem. Ber. 95, 246-8, 1962]. However, toxicity and corrosive character of fluorosulfonic acid are major drawbacks of this synthesis. Moreover, yield of the reaction can fluctuate strongly for several experiments. An other process implied reaction of $(ClSO_2)_2NH$ ("HClSI") with AsF_3. $(FSO_2)_2NH$ is further isolated after treatment of bulk media by NaCl in dichloromethane [Ruff & Lustig, Inorg. Synth. 1968, 11, 138-43]. This process is of poor interest due to the high price of AsF_3 and its toxicity.

From this acid, the preparation of its lithium salt is also difficult. Contrary to $LiPF_6$, it is possible to prepare lithium salt of HFSI ("LiFSI") in water solution from the acid and a lithium source such as lithium carbonate. However, on drying, it is impossible to abstract the last molecules of water without decomposing major part of the lithium salt, this is specific to the lithium cation due to the high reticular energy of LiF. WO95/26056 described a process to produce LiFSI by reacting $(FSO_2)_2NH$ and LiF in an aprotic solvent, such as acetonitrile. This process present several drawbacks, first the stability of the solvent to strong acid and it is also rather difficult to dry the obtained slurry to obtain pure LiFSI as there is a strong interaction between the lithium salt and acetonitrile solvent.

WO02/053494 describe a process to prepare monovalent salt of HFSI by a "Halex" process in aprotic solvents. Such process is mainly designed to obtain the potassium salt of HFSI ("KFSI"). LiFSI salt preparation is also described but lead to the formation of a LiFSI salt containing large amount of impurity such as FSO_3Li.

In the case of phosphoryl derivatives, the reaction of $LiN(SiMe_3)_2$ with POF_3 lead to the formation of $LiN(POF_2)_2$ after

elimination of volatile Me_3SiF [Fluck & Beuerle, Z. Anorg. Allg. Chem. 412(1), 65-70, 1975]. However, this process used costly silyl derivatives and toxic gaseous POF_3. So, it is clear this laboratory process is far from an industrial one's, moreover the final product contains undesirable Me_3SiF complex with the salt which is difficult to remove. Moreover, this synthesis is of a limited scope.

Unfortunatly, it appears there is no satisfactory industrial process to produce anhydrous lithium imides salts, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical such as $(FSO_2)_2NLi$ or $(F_2PO)_2NLi$, and more generally to produce their acid precursors.

3. Description of the invention:

To overcome those difficulties of salt preparation such as LiFSI, research has been done on various synthetic pathways, such as for example lithiation of the acid by alkyllithium in anhydrous alcane solvent. In fine, as a result of extensive investigations, a process based on anhydrous HF chemistry has been designed as the most suitable industrial synthetic procedure for anhydrous lithium imides salts, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical and characterized in that the fluorine atoms are covalently bond to the sulfur or phosphorus atoms, such as $(FSO_2)_2NLi$ or $(F_2PO)_2NLi$. As a result of research activities on lithium salt preparation, anhydrous HF chemistry has also proved effective to produce their acids counterparts.

So, the basic description of the process illustrated in the case of LiFSI is illustrated below:

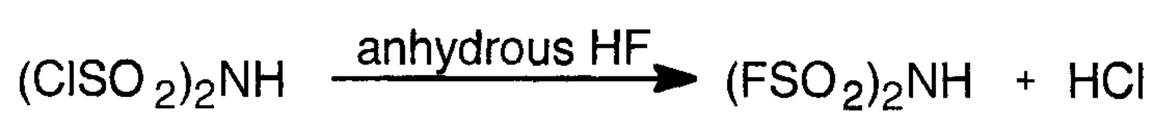
$$(FSO_2)_2NH + LiF \xrightarrow{\text{anhydrous HF}} (FSO_2)_2NLi + HF$$

Indeed, the process to obtain an anhydrous lithium salt consist of an acid-base reaction between an acid imide, containing fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical, and a base LiM used as lithium

cation source, preferably choose such as the HM species, formed during lithiation of the imide, is volatile as with LiCl or LiF which produce HCl and HF.

For example when operated at 180°C in an autoclave, this reaction lead to the formation of LiFSI of good purity.

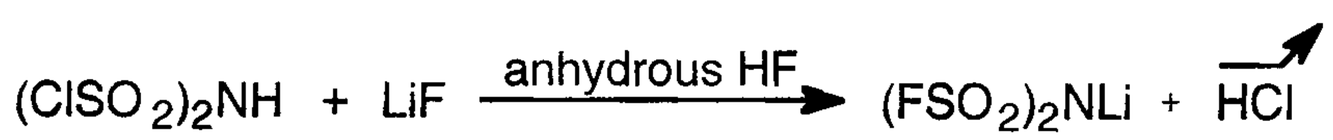
The R&D activities on fluorinated imide lithium salt preparation as also allows to design an efficient process to obtain their acid counterparts from their chlorine derivatives in anhydrous HF, i.e from imides containing chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor radical and characterized in that the chlorine atoms are covalently bond to the sulfur or phosphorus atoms, such as $(ClSO_2)_2NH$ or $(Cl_2PO)_2NH$. This process is illustrated below in the case of bis(fluorosulfonyl)imide (HFSI):



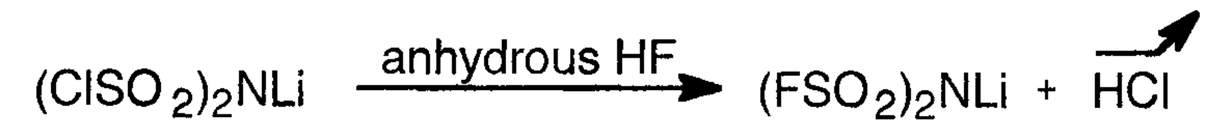
Indeed, the fluorinated acid is obtained by a chlorine/fluorine exchange operated in anhydrous HF. It may be necessary to distillate the bulk media after reaction to obtain the pure acid.

The effectiveness of such reaction is non-obvious, it has been showed that when operated in an autoclave, the reaction proceed efficiently at temperature reaching or above 60°C. The anhydrous HF was then evaporated and the resulting product distillated to obtain pure HFSI.

It is also possible by a combination of both processes to obtain directly lithium salt such as LiFSI from the chlorine counterpart:



An other possibilities is to obtain directly lithium salt such as LiFSI from the lithiated chlorine counterpart:



The availability of acid imide containing (FSO_2-) or (F_2PO-) electroattractor radical from their chlorine equivalent ($ClSO_2$-) or (Cl_2PO-) radical is particularly useful as it allows to extend the scope of available precursor to produce lithium imide salt containing (FSO_2-) or (F_2PO-) radical.

It has also been put in evidence that HFSI could be obtained from HClSI by bulk reaction with KHF_2.

The present invention is illustrated by the following examples, which are only used as an illustrative purpose without intended to provide any limitation for man of the art.

Preparation of HFSI: Reaction of 1 gr $HN(SO_2Cl)_2$ with 4 gr HF in an autoclave was done as various temperatures. Results are resumed in Table 1. It appears that an efficient Cl/F exchange could be performed. After evaporation of HF and distillation of bulk media, pure HFSI is obtained in a yield of at least 50%.

Time (hours)	Temperature	Yield
12	RT	0%
24	RT	0%
12	30	3-5%
12	50	7-10%
4	110	24%
7	120	50%
5	120	55%
2	130	55%

Table 1: Synthesis of HFSI in HF

Preparation of HFSI: Reaction of 1 gr $HN(SO_2Cl)_2$ with 10 gr HF in an autoclave was done as various temperatures. It appears that an efficient Cl/F exchange is performed at 60°C and above after 2 hours reaction. After evaporation of HF and distillation of bulk media, pure HFSI is obtained in a yield

of at least 50%. The reaction was also performed in gas phase with a yield of at least 50%. The reaction was also performed with $CF_3SO_2NHSO_2Cl$ and FSO_2NHSO_2Cl, ^{19}F NMR show fluorine pic relative to HFSI and $CF_3SO_2NHSO_2F$ after distillation of reactive media.

Preparation of FSI: Reaction of 10 gr $HN(SO_2Cl)_2$ with 5 KHF_2 equivalents was performed in bulk at 100-160°C in Teflon recipient under argon. After three hours, a sample of reaction media in CD_3CN was analyzed by ^{19}F NMR, showing a peak characteristic of the $(FSO_2)_2N^-$ anion.

Preparation of HFSI: Reaction of 10 gr $HN(SO_2Cl)_2$ with 4 gr HF in an autoclave was done. Reaction mixture without chlorine traces were obtained at 65-70°C temperatures. After distillation, product obtained was identified by ^{19}F NMR as $HN(SO_2F)_2 \cdot HF$ adduct.

Preparation of LiFSI: Reaction of 1 gr of $HN(SO_2F)_2$ and an equimolar quantity of LiF in 5 ml of HF, at 180°C during 1 hour in an autoclave, gave nearly quantitative yield of LiFSI (> 99%) contaminated with a small amount of $LiOSO_2F$ - as determined by ^{19}F NMR.

Preparation of LiFSI: Reaction of 1 gr $HN(SO_2Cl)_2$ with 364 mg LiF in an autoclave containing 10 ml of HF was done at 120°C during two hours. ^{19}F NMR show a peak characteristic of the $(FSO_2)_2N^-$ anion and ^1H NMR no peak characteristic of acidic proton in HFSI. The reaction was also performed with $CF_3SO_2NHSO_2Cl$, ^{19}F NMR show fluorine pic relative to $CF_3SO_2N^-SO_2F$ anions.

Preparation of LiFSI: Reaction of 1 gr $LiN(SO_2Cl)_2$ with 400 mg LiF in an autoclave was done at 100°C during two hours. ^{19}F NMR show a peak characteristic of the $(FSO_2)_2N^-$ anion.

Claims:

1) A process to prepare an anhydrous imide lithium salt LiX obtained by reaction in anhydrous hydrogen fluoride (HF) of an acid imide HX, containing at least one fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor radical and characterized in that the fluorine atoms are covalently bond to the sulfur or phosphorus atoms, with a base LiM.

2) A process according to claim 1 characterized in that the conjugated acid HM of LiM is volatile.

3) A process according to claim 1 characterized in that LiM is LiCl or/and LiF.

4) A process according to claim 1 characterized in that HX is HNZ_1Z_2 where Z_1 is a fluorosulfonyl (FSO_2-) or fluorophosphoryl (F_2PO-) electroattractor and Z_2 is an electroattractor radical with a Hammett parameter σ_P superior to 0.4, including FSO_2- and F_2PO- radicals.

5) A process according to claim 4 characterized in that Z_2 is choose from FSO_2-, F_2PO- or $C_nF_{2n+1}SO_2$- with n = 1-10.

6) A process according to claim 5 characterized in that $1 \leq n \leq 4$.

7) A process according to claim 4 characterized in that HX is $(FSO_2)_2NH$.

8) A process according to claim 1 characterized in that the reaction is performed between 25 and 200°C.

9) A process according to claim 8 characterized in that the reaction is performed between 50 and 150°C.

10) A process according to claim 4 characterized in that the reaction is performed in an autoclave.

11) A process to prepare an acid imide HX' obtained by a chlorine/fluorine exchange, perform in and by anhydrous HF, from an acid imide HX', containing at least one chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor radical and characterized in that the chlorine atoms are covalently bond to the sulfur or phosphorus atoms.

12) A process according to claim 11 characterized in that HX' is $HNZ'_1Z'_2$ where Z'_1 is a chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor and Z'_2 is an electroattractor radical with a Hammett parameter σ_P superior to 0.4, including $ClSO_2$- and Cl_2PO- radicals.

13) A process according to claim 12 wherein Z'_2 is $ClSO_2$-, Cl_2PO- or $C_nF_{2n+1}SO_2$- with n = 1-10.

14) A process according to claim 12 where HX' is $(ClSO_2)_2NH$.

15) A process according to claim 12 characterized in that the reaction is performed between 25 and 200°C.

16) A process according to claim 15 wherein the reaction is performed between 50 and 150°C.

17) A process according to claim 12 characterized in that the reaction is performed in an autoclave.

18) A process according to claim 12 characterized in that the reaction is performed in gaseous phase.

19) A process according to claim 12 characterized in that the reaction media is distillate to obtain pure HX acid.

20) A process to prepare an anhydrous lithium imide salt LiX' obtained by a chlorine/fluorine exchange and H^+/Li^+ exchange, perform in and by anhydrous HF in presence of a lithium salt LiM, from an acid imide HX', containing at least one chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-)

electroattractor radical and characterized in that the chlorine atoms are covalently bond to the sulfur or phosphorus atoms.

21) A process according to claim 20 characterized in that the conjugated acid HM of LiM is volatile.

22) A process according to claim 21 characterized in that LiM is LiCl or/and LiF.

23) A process according to claim 20 characterized in that LiM is in equivalent molar quantity of HX'.

24) A process according to claim 20 characterized in that HX' is $HNZ'_1Z'_2$ where Z'_1 is a chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor and Z'_2 is an electroattractor radical with a Hammett parameter σ_p superior to 0.4, including $ClSO_2$- and Cl_2PO- radicals.

25) A process according to claim 24 characterized in that Z'_2 is choose from $ClSO_2$-, Cl_2PO- or $C_nF_{2n+1}SO_2$- with n = 1-10.

26) A process according to claim 25 characterized in that $1 \leq n \leq 4$.

27) A process according to claim 24 characterized in that HX' is $(ClSO_2)_2NH$.

28) A process according to claim 20 characterized in that the reaction is performed between 25 and 200°C.

29) A process according to claim 28 characterized in that the reaction is performed between 50 and 150°C.

30) A process according to claim 24 characterized in that the reaction is performed in an autoclave.

31) A process to prepare an acid imide HX' obtained by a chlorine/fluorine exchange, perform by KHF_2, from an acid imide HX', containing at least one chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor radical and characterized in that the chlorine atoms are covalently bond to the sulfur or phosphorus atoms.

32) A process according to claim 31 characterized in that HX' is $HNZ'_1Z'_2$ where Z'_1 is a chlorosulfonyl ($ClSO_2$-) or chlorophosphoryl (Cl_2PO-) electroattractor and Z'_2 is an electroattractor radical with a Hammett parameter σ_P superior to 0.4, including $ClSO_2$- and Cl_2PO- radicals.

33) A process according to claim 32 wherein Z'_2 is $ClSO_2$-, Cl_2PO- or $C_nF_{2n+1}SO_2$- with n = 1-10.

34) A process according to claim 32 where HX' is $(ClSO_2)_2NH$.

35) A process according to claim 32 characterized in that the reaction is performed between 25 and 200°C in bulk.

36) A process according to claim 35 wherein the reaction is performed between 50 and 150°C in bulk.

36) A process according to claim 32-36 characterized in that the reaction is performed in presence of a solvent.

37) A process according to claim 32 characterized in that the reaction is performed in an autoclave.

38) A process according to claim 32 characterized in that the reaction is performed in gaseous phase.

39) A process according to claim 32 characterized in that the reaction media is distillate to obtain pure HX acid.